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THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, April 13, 1949, with the President, Mr E. A. Evans, in the Chair.

The Minutes of the preceding Ordinary General Meeting, held on March 9, 1949, were read, confirmed, and signed.

The General Secretary (D. A. Hough) announced the elections to membership since the previous Ordinary General Meeting.

The General Secretary gave notice that an Ordinary General Meeting of the Institute would be held on May 11, when Dr F. Morton would present a paper on " Examination of Crude Oils in Relation to Geological Formations "; and that the Annual General Meeting of the Institute would be held in the hall of the Royal Society of Arts, Adelphi, London, W.C.2, on April 27 at 4.30 p.m., followed by the delivery of the Presidential Address at 5.30 p.m.

The President: This evening we have the pleasure to welcome Mr S. G. Daniel. You will perhaps remember that in January, when Messrs Barwell and Milne presented their paper on the measurement of kinetic boundary friction, Mr Daniel was one of three gentlemen who came from Cambridge to listen. Mr Daniel has been for eight years a member of the research staff of the Thornton Research Centre, and for the last eighteen months he has been working with Dr Bowden at Cambridge on subjects which are extremely familiar to all of us.

This evening he will not speak of his work at Cambridge, but of the work he was doing when he was at Thornton. The subject he has chosen is that of the viscosity of aero-engine oils at low temperatures. I think that, when you hear him present his paper, you will recognize the importance of this work during the war years and how necessary it has become to release the information, for I am sure it will clarify some of the problems which have been worrying us.

Therefore, I have much pleasure in inviting him to present his paper.

Mr Daniel presented the following paper :—

THE VISCOSITY OF AERO-ENGINE OILS AT LOW TEMPERATURES.

By S. G. DANIEL.

SUMMARY.

This paper describes the construction and operation of a viscometer designed to measure the viscosity of high-duty aircraft lubricating oils at shearing stresses of up to 45,000 dynes/sq. cm. and at temperatures between 20° and −25° C. The results obtained indicate the type of anomalous viscosity effects which may be anticipated at low temperatures and show that they are due to the deposition of wax or other solid hydrocarbons from the oil. The magnitude of these effects appears to be related to the crystal size of these solid hydrocarbons and to the amount present. However, the relationship is very complex, and further work of a more fundamental nature is necessary before any quantitative relation can be expressed. The influence of a pour-point depressant upon the low-temperature flow properties of an oil is also described, together with a brief discussion of the bearing these results have upon the cold-starting lubrication of aero-engines.

INTRODUCTION.

DIFFICULTIES associated with the handling of aviation lubricants and the cold starting of aircraft engines at the low temperatures encountered in Canada, Alaska, and elsewhere, have caused much attention to be given to methods of improving the fluidity of oils at low temperatures. It is well known that the increase in viscosity with lowering of the temperature is predictable from the viscosity index or from the A.S.T.M. viscosity–temperature charts down to the temperature at which wax crystals form, and the A.S.T.M. pour point has constituted a useful relative measure of the tendency of undisturbed oils to flow under their own head for a given rate of cooling. In fact, the pour point has been considered to predict approximately the "channelling" characteristics [1] of diluted aircraft oils, although other work [2, 3, 4] indicates that the validity of this conclusion is limited. The channelling of oil in aircraft tanks and at pump entries, due to the inability of oil to flow under its own head, has been one of the major difficulties encountered in cold climates. Increase of frictional losses in moving engine components due to excessive viscosity has also been responsible for increasing starting torques at low temperatures.

As a complementary laboratory investigation to a programme of cold-starting tests on various aero-engines, a study of the viscous behaviour of aircraft oils at low temperatures was made, and the influence of factors such as dilution with gasoline, shearing stress, rate of cooling, and the addition of pour-point depressants on the measured viscosity was examined. With a background of such physical data, it was hoped that the engine data might be more adequately analysed and useful predictions made about oil performance at low temperatures under specific conditions. This paper gives an account of the methods used and the results obtained while examining the viscous behaviour of aircraft oils at low temperatures.

Newtonian and non-Newtonian Liquids.

Since this paper concerns the flow properties of liquids which do not show Newtonian behaviour, it is convenient at this point to give a brief account of the terms employed in describing the behaviour of non-Newtonian liquids. A Newtonian liquid is, of course, a liquid for which the viscosity coefficient is constant irrespective of the rate of shear or shearing stress. Its absolute viscosity is defined by :

$$\eta = \frac{S}{R}$$

where η = viscosity (poises);
S = shearing stress (dynes/sq. cm.);
R = rate of shear (sec^{-1}).

In the case of a liquid flowing through a capillary, its viscosity is given by the Poiseuille equation :

$$\eta = \frac{P\pi a^4}{8EL} = \frac{\frac{Pa}{2L}}{\frac{4E}{\pi a^3}} = \frac{S_a}{R}$$

where P = pressure difference between the end of the capillary (dynes/sq. cm.);
a = radius of the capillary (cm);
L = length „ „ „ (cm);
E = rate of efflux (ml/sec);
$S_a = \frac{Pa}{2L}$ = shearing stress at wall of capillary (dynes/sq. cm.);
$R = \frac{4E}{\pi a^3}$ = rate of shear at „ „ „ (sec^{-1});

Thus, with a Newtonian liquid the plot of P against E is a straight line for a given capillary.

There are many liquids and colloidal solutions which do not show Newtonian flow characteristics, but those viscosity changes with the applied rate of shear or the shearing stress. In such cases the above equations do not give the true viscosity of the liquid, but the equations may be used to calculate an apparent viscosity for each rate of shear and shearing stress. The apparent viscosity of a liquid is the viscosity of a Newtonian liquid which would flow at the same rate as the non-Newtonian liquid under the same conditions.

Materials which possess non-Newtonian flow characteristics are often divided into two main groups—namely, viscous materials and plastic materials. The principal characteristic of viscous flow is that the slightest shear causes flow, while plastic materials possess a yield value. Yield value may be defined as the minimum tangential force per unit area necessary to cause flow; if a force greater than the yield value is applied to a plastic material, then it will flow, but the rate of flow is not directly proportional to the applied stress.

Several workers have developed methods for calculating the absolute

viscosity of this type of material from data obtained by measurements upon flow through capillary tubes, and these methods are discussed later.

In addition to the above phenomena, there are two other properties of non-Newtonian materials which tend to upset viscosity measurements; these are slip and thixotropy. Slip can occur at the walls of a capillary tube while a liquid is flowing, and measurements taken while this is occurring would lead to values of the viscosity which are too low. For a thixotropic substance, the viscosity varies with the time during which the substance is subjected to the shearing stress. The term thixotropy has been used in a far wider sense, and is often applied to a liquid the viscosity of which is changed with the applied rate of shear. In this paper, the original definition will be retained.

The rate of shear in an oil film between the sliding components of an engine is many times greater than that involved in the normal measurement of the viscosity of an oil in a viscometer. As long as the oil shows Newtonian behaviour, the viscosity at a low rate of shear is the same as that at higher rates of shear (except perhaps in certain exceptional circumstances which need not be discussed here). From the work of other investigators [5] it is clear that at low temperatures oils cease to be Newtonian liquids. Hence, in order to analyse engine data it was decided to measure the viscosity of oil at low temperatures at various rates of shear. Measurements at low rates of shear were carried out in Ubbelohde viscometers, and measurements at higher rates of shear in a specially designed viscometer in which pressures up to 100 p.s.i. were applied in forcing oil through a capillary.

Owing to the fact that the Ubbelohde viscometers were calibrated to give kinematic viscosity, while the pressure viscometer gave results in absolute units, it was also necessary to measure the density of the oils at the temperatures employed. Conversion of absolute units to kinematic units was made by the use of the formula

$$\text{Kinematic viscosity (stokes)} = \frac{\text{absolute viscosity (poises)}}{\text{density}}.$$

Section I. Low-temperature Viscosity at Low Shearing Stresses.

For comparison with the viscosities which were determined at high shearing stresses and are described later, this section summarizes low-temperature viscosity data obtained using suspended-level Ubbelohde viscometers for aero-engine oils, both undiluted and diluted with 100-octane aviation gasoline. In these viscometers flow occurs through a capillary tube under a pressure which is never more than a few inches of oil, and the shearing stresses and rates of shear are therefore comparatively low.

Experimental Details.

In order to carry out the measurements at low temperatures, a thermostat was constructed for use at any temperature between 20° and −60° C. A diagram of the arrangement is shown in Fig. 1.

The thermostat consisted of a glass vessel 6 in diameter and 14 in high, which, except for an observation window, was heavily lagged with felt ($\frac{1}{2}$ in thick). On account of the high solubility of water in ethyl alcohol at low temperatures, ethyl alcohol was chosen for the thermostatting liquid. Efficient circulation was maintained by the pumping arrangement shown, together with a small stirring motor not shown in the diagram. Alcohol leaving the pump passed back to the thermostat either directly or via a spiral coil of piping immersed in a cooling tank. The cooling tank was heavily lagged with asbestos and contained a mixture of methyl ethyl ketone and solid carbon dioxide at −80° C. All piping was lagged with asbestos string. By closing gate valve A and opening B fully, the liquid in the bath could be brought to a temperature of −20° C in 15 min and to −50° C in 40 min. When the bath had reached the desired temperature,

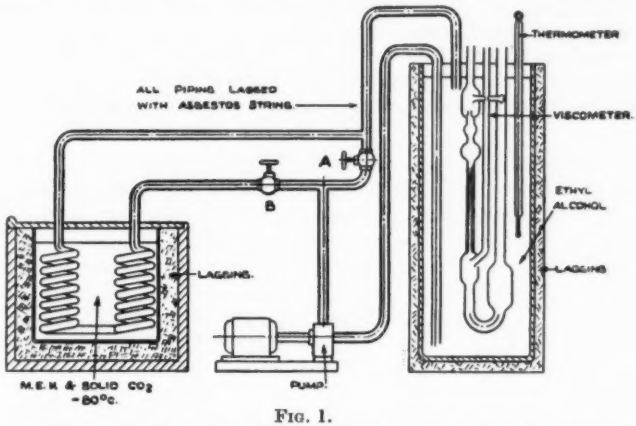

FIG. 1.

COOLING ARRANGEMENT FOR VISCOSITY DETERMINATIONS AT LOW TEMPERATURES.

gate valve B was partially closed and A partially opened, until after a few minutes the positions of the valves were found at which the temperature of the bath remained practically constant, so long as the cooling tank was maintained at −80° C by the addition of further quantities of solid carbon dioxide. It was found that, after equilibrium had been established, the temperature of the bath could be maintained constant, by slight adjustment of the gate valves, to within less than ±0·1° C for periods of up to 2 hr.

Owing to this slight temperature variation, the viscosity measurements carried out were liable to an error of 2 to 3 per cent, but, as will be seen later, this is small compared with the large differences between the measured viscosity and the extrapolated value at low temperatures.

Viscosities were measured in modified suspended-level Ubbelohde viscometers as described in " Standard Methods for Testing Petroleum and its Products " (7th edn., 1946, p. 458) and, in order that the results might be strictly comparable, all measurements below 10° C were carried out in the same viscometer.

The temperature of the bath between 25° and −38° C was measured by a mercury-in-glass thermometer graduated in 1/5° C, and below −38° C by a copper–constantan thermocouple calibrated at the freezing point of pure carbon tetrachloride, chlorobenzene, methyl aniline, *m*-xylene, and chloroform. The lowest temperature at which the bath could be conveniently maintained for long periods was −50° C.

Experimental Results.

(a) *DTD.109 and DTD.472B Oils.*

The viscosities of five oils * were measured at 5° C intervals down to a temperature at which the flow times became excessively long. The bath was cooled at a rate of about 5° C in 10 min between test temperatures, and the oil allowed to stand at this temperature for 20 min to ensure uniform temperature distribution before measurements were carried out. The results obtained are given in Table I; between 20° and −5° C the results given are the mean of three successive determinations, but below −5° C only one determination was made owing to the long flow time.

Table I.

Viscosity of DTD.472B and DTD.109 Oils at Low Temperatures.

Oil.	Viscosity.							
	A.		B.		C.		D.	E.
Temp, ° C.	Stokes.	Poises.	Stokes.	Poises.	Stokes.	Poises.	Stokes.	Stokes.
60	0·822	—	0·781	—	0·799	—	0·816	0·836
25	6·072	5·365	5·922	5·195	6·109	5·389	—	7·191
20	8·882	7·875	8·646	7·612	8·818	7·805	8·955	10·64
15	13·61	12·11	13·02	11·50	13·11	11·64	—	—
10	20·12	17·96	19·77	17·52	20·03	17·85	20·31	26·25
5	33·50	30·0	32·60	29·0	32·45	29·01	32·90	—
0	55·80	50·2	55·26	49·3	52·55	47·1	55·26	76·35
− 5	98·3	88·7	106·6	95·5	90·0	81·0	97·50	137·7
−10	240	217	224	201	158	143	169	272
−15	>1950	>1770	>1620	>1460	341	309	>404	674
−20	No flow	No flow	No flow	No flow	No flow	No flow	No flow	>3900
−25	—	—	—	—	—	—	—	No flow
Pour point, ° C	−12	−12	−12	−12	−15	−15	−15	−18

Viscosities at 25° and 60° C were measured in the thermostats used for normal routine measurements.

(b) *Blends of 100-octane Fuel † and Oil A.*

The viscosities of 10, 20, and 30 per cent by vol blends of 100-octane fuel in oil A were determined in the same way as for the undiluted oils. The results obtained are given in Table II, together with the results for oil A for comparison.

* Four of these oils, A, B, C, and D conformed to the Air Ministry Specification DTD.472B, while E conformed to the specification DTD.109.

† The physical properties and the hydrocarbon analysis of the 100-octane fuel are given in the appendix.

TABLE II.

Viscosity of Blends of Oil and 100-Octane Fuel at Low Temperatures.

Blend.	Viscosity.							
	Oil A.		A + 10% vol 100-octane fuel.		A + 20% vol 100-octane fuel.		A + 30% vol 100-octane fuel.	
Temp, °C.	Stokes.	Poises.	Stokes.	Poises.	Stokes.	Poises.	Stokes.	Poises.
20	8·882	7·875	2·20	1·92	0·607	0·596	0·288	0·242
10	20·12	17·96	4·27	3·75	1·22	1·05	0·437	0·370
0	55·80	50·15	9·16	8·09	2·29	1·99	0·717	0·612
− 5	98·3	88·7	14·2	12·6	—	—	—	—
−10	240	217	22·7	20·2	4·71	4·12	1·28	1·10
−15	1,950	1,770	42·0	36·9	7·19	6·32	—	—
−20	No flow	No flow	131	118	12·0	10·6	2·45	2·13
−25	—	—	3,960	3,570	22·6	20·0	3·63	3·16
−30	—	—	No flow	No flow	63·3	56·3	5·76	5·04
−35	—	—	—	—	352	315	10·2	8·96
−40					Flow very slow	Flow very slow	21·6	
−45	—	—	—	—	—	—	50·1	—
−49	—	—	—	—	—	—	113	—
Pour point, ° C	−12	−12	−23	−23	−43	−43	−48	−48

At temperatures less than 10° C above the pour point of these blends the viscosity was not reproducible, and the flow time decreased with each successive determination at any temperature. Similar results, obtained with solutions of wax in medicinal paraffin, are discussed later. When such effects occurred, the value of the viscosity given in Table II is that obtained from the first determination, since this indicates the extreme value which may be encountered when the results are considered in connexion with the cold starting of aircraft engines.

(c) *Influence of Rate of Cooling.*

DTD.472B Oils. In the case of the DTD.472B oils, it was thought that a rate of cooling of 5° C in 10 min between measurements might give rise to chilling of the oil. However, a few measurements made with intervals of cooling at 10° C per hour, were not significantly different from those carried out at the more rapid rate of cooling. In order to save time, the more rapid rate of cooling was used in obtaining the results given in Tables I and II. Rates of cooling more rapid than 5° C in 10 min were found to increase the viscosity of undiluted oils at temperatures below 0° C, while plunging a viscometer containing oil at room temperature into a bath at temperatures of −5° C and below, resulted in very long flow times due to the sudden chilling (" shock-cooling ") of the oil.

Diluted Oils. Experiments showed that the rate of cooling at temperatures above the pour point was more important in the case of diluted oils than with undiluted oils. Some typical results are shown in Table III.

Other blends of oil A and 100-octane fuel behaved in a similar way at temperatures of between 0° and 15° C above their pour point. It appears from the results that rates of cooling slower than 0·5° C/min do not influence the viscosity of the blends.

TABLE III.

Influence of Cooling Method on Measured Viscosity of Oil–Gasoline Mixture.

Blend.	Temp, ° C.	Viscosity, stokes.	Cooling treatment.
Oil A + 20% vol 100-octane fuel	−25	22·6	Cooled 0·5° C/min; temperature maintained constant for 10–20 min at each 5° C interval.
,,	−25	22·6	Cooled 2° C/min; temperature maintained constant for 10–20 min at each 5° C interval.
,,	−25	29·9	Cooled steadily to −25° C in 25 min.
,,	−25	68·4	Oil at 20° C plunged into bath at −25° C
,,	−30	53·2	Cooled at 2·5° C/min; temperature maintained constant for 10–20 min at each 5° C interval.
,,	−30	Practically no flow.	Oil at 20° C plunged into bath at −30° C.

(d) *Effect of Storage.*

The viscosity of blends of oil A and 100-octane fuel at low temperatures was found to be dependent upon the time of storage at room temperature. Some typical results for a blend of oil A + 20 per cent 100-octane fuel at −25° C are shown in Table IV. It is of interest to note that similar increases in viscosity at low temperatures have been noted during the examination of certain hydraulic oils at these laboratories.

TABLE IV.

Influence of Storage History upon Measured Viscosity.

Oil : A + 20% vol 100-octane fuel
Temp : −25° C

Storage period (at approx 20° C).	Cooling treatment.	Viscosity, stokes.
Nil	Shock cooled	33·8
8 days without agitation	,, ,,	53·7
12 ,, ,, ,,	,, ,,	113·7
21 ,, ,, ,,	,, ,,	201·0
8 days; thoroughly shaken before pouring into viscometer	Shock cooled	39·5
21 days; thoroughly shaken before pouring into viscometer	,, ,,	41·6
Nil	Cooled at 2° C/min; temp maintained constant for 10–20 min for viscosity determination	22·1
10 days without agitation	As above	22·4
21 ,, ,, ,,	,, ,,	22·7
10 days without agitation	As above, but without viscosity determination each 5° C	20·7

The viscosity of the shock-cooled blend increased with the time of storage, while blends cooled slowly gave no such viscosity increase with storage time. When a blend was thoroughly shaken before filling the viscometer, the high viscosity on shock cooling was largely destroyed. Similar results were obtained with other blends of oil A and 100-octane fuel at various temperatures.

Discussion of Results.

The relation

$$\log T = k \log \log (\eta + 0{\cdot}6) + c \quad . \quad . \quad . \quad . \quad (1)$$

where T = absolute temperature (°K);
η = kinematic viscosity (centistokes);
and k and c are constants for a given oil;

has been extensively used to represent the change of viscosity of oil with temperature, and is the basis of the A.S.T.M. Tentative Viscosity Tempera-

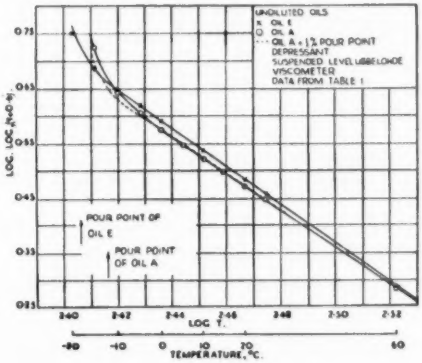

Fig. 2.

DEVIATION FROM RELATION LOG $T = K$ LOG. LOG $(\eta + 0{\cdot}6) + C$ AT LOW TEMPERATURES.

ture charts (D.341–39). It is stated [6] that provided the oil remains a homogeneous liquid of constant composition, then the plot of log T against log log $(\eta + 0{\cdot}6)$ is a straight line.

In Fig 2, the results from Table I for oils A and E are plotted in this manner; it is seen that the linear relation holds within experimental error down to temperatures within 10° C of the pour point. At lower temperatures than this the viscosity is greater than equation (1) would predict, the discrepancy rapidly becoming greater as the temperature becomes lower. In Fig. 3 the results from Table II have been plotted in a similar manner. The addition of fuel to the oil affects only slightly the temperature at which deviation from equation (1) occurs, while it has a considerably greater effect on the pour point. It is also evident from this graph that the deviation of the measured viscosity from the value obtained from equation (1) by extrapolation is reduced by the addition of fuel at any temperature.

In order that the differences between the oils may be presented more clearly, the results from Tables I and II have been plotted in a rather different manner. From the linear $\log T - \log\log(\eta + 0{\cdot}6)$ plot, extra-

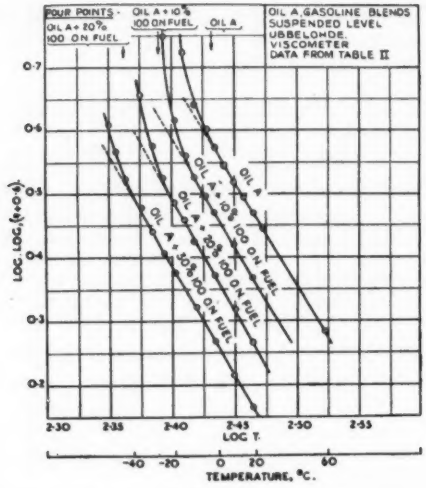
POUR POINTS
OIL A + 20% 100 ON FUEL
OIL A + 10% 100 ON FUEL
OIL A
OIL A, GASOLINE BLENDS
SUSPENDED LEVEL
UBBELOHDE VISCOMETER
DATA FROM TABLE II
OIL A
OIL A + 10% 100 ON FUEL
OIL A + 20% 100 ON FUEL
OIL A + 30% 100 ON FUEL
LOG LOG (η+0·6)
LOG T.
TEMPERATURE, °C.

FIG. 3.

DEVIATION FROM RELATION LOG $T = K$ LOG. LOG $(\eta + 0{\cdot}6) + C$ AT LOW TEMPERATURES.

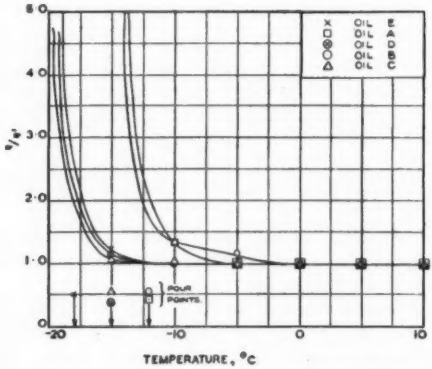

FIG. 4.

η/η' V. TEMPERATURE FOR DTD. 109 AND DTD.472B OILS AT LOW TEMPERATURES.

polated values of the viscosity η' at low temperatures are deduced; this is equivalent to using A.S.T.M. Chart D.341–39 to predict viscosity at low temperatures. The ratio of the measured viscosity to the "predicted" extrapolated viscosity $\left(\frac{\eta}{\eta'}\right)$ is then calculated, and in Figs. 4 and 5 this ratio

is plotted against its corresponding temperature. Thus so long as equation (1) holds for the oil $\eta/\eta' = 1{\cdot}00$, but when the equation ceases to hold at low temperatures η/η' becomes greater than unity. For all the oils examined, η/η' becomes greater than unity at some temperature which lies a few degrees above the pour point. Below this temperature the ratio η/η' rapidly increases above unity.

Assuming that equation (1) does hold so long as only one phase is present in the oil, then it would appear that at some temperature just above the pour point, when η/η' becomes greater than unity, a phase change occurs in the oil. The most probable change likely to occur is the separation of solid hydrocarbons from the liquid oil. It was significant that the oil became cloudy at the same temperature as that at which the ratio η/η' exceeded unity. Further evidence that a phase change occurred was obtained in a number of ways which are discussed later in the paper.

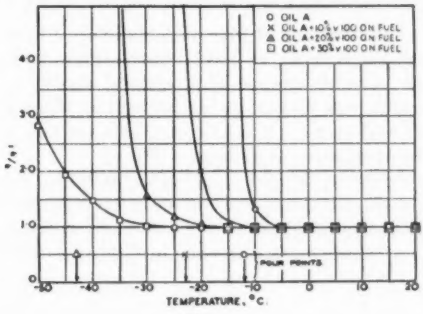

FIG. 5.

η/η' V. TEMPERATURE FOR BLENDS OF 100-OCTANE FUEL AND OIL A AT LOW TEMPERATURES.

The influence of the rate of cooling upon viscosity appears to be connected with crystal size of the solid hydrocarbons separating out of solution. Some experiments with a waxy raffinate (described later) showed that rapid cooling gave rise to the formation of a large number of small crystals of wax, while slow cooling gave a smaller number of comparatively large crystals. The oil containing the small crystals was found to have a viscosity many times greater than that of the oil containing the large crystals at the same temperature. It is probable that the high viscosity of the rapidly cooled oil is due to the interlocking of the small crystals to form some loose type of network extending throughout the bulk of the oil and interfering with the flow of the oil. The larger crystals do not interlock to the same extent and so have less influence upon the flow of the oil. Doubtless, with DTD.472B oils and diluted blends, similar effects come into play and account for the high viscosity obtained by rapid cooling.

The increase in viscosity upon storage is probably also due to the presence of solid hydrocarbons, although the actual mechanism of the phenomenon is not at all clear. The fact that increased viscosity can only be obtained by rapid cooling after undisturbed storage, and not by slow cooling of the

oil, implies the development in the oil at the storage temperature of some type of structure which can be destroyed by agitation and which does not influence the viscosity at normal temperatures. This structure must gradually change when the oil is cooled slowly, but with rapid cooling this structure would be "frozen" and still exist at low temperatures.

As stated earlier, similar effects were found during the examination of some hydraulic oils. These effects were found to be associated with the presence of very small quantities of wax. When this wax was removed these effects no longer occurred, while undisturbed storage of the oil at temperatures above the melting point of the wax entirely eliminated this effect.

It is probable, then, that small quantities of wax are responsible for these effects in the gasoline–oil blends. Unfortunately, owing to the high volatility of the gasoline, it was not convenient to carry out storage tests at higher temperatures with simple apparatus.

(e) *Viscosity of Medicinal Paraffin Containing Dissolved Wax.*

It was found that solutions of wax in medicinal oil were capable of giving rise to viscosity phenomena at low temperatures very similar to those obtained with the aircraft-engine oils described above.

Medicinal paraffin was chosen as the solvent in these experiments, since it was wax free and gave a straight-line plot on the A.S.T.M. viscosity chart down to temperatures of at least −20° C.

1 and 0·25 per cent by weight solutions of paraffin wax (m.p. 55–58° C) in medicinal oil were prepared, and viscosity determinations made on these solutions and on the original oil at 5° C intervals between 25° and −15° C at the same rate of cooling as for the oils in Table I. The results are shown in Table V.

TABLE V.

Viscosity of Paraffin Wax Solutions in Medicinal Oils.

Temperature, ° C.	Viscosity of oil, stokes.		
	Medicinal oil.	+0·25% wt wax.	+1% wt wax.
25	1·63	1·62	1·56
20	2·32	2·31	2·23
15	3·40	3·36	3·69 *
10	5·02	4·94	6·63
5	7·70	7·66	10·5
0	12·4	20·1 *	20·1
− 5	20·1	30·5	42·7
−10	35·3	58·8	110·0
−15	67·8	—	Practically solid

* Oil became opaque.

As was expected, as long as the wax was in solution, the viscosity of the wax solutions was slightly less than that of the medicinal oil at the corresponding temperature, but as soon as wax began to be thrown out of solution (indicated by the onset of opacity) the viscosity suddenly increased above that of the medicinal oil. It is obvious from these results that the presence of quite small quantities of wax in an oil has a great influence upon the viscosity of that oil at low temperatures.

As in the case of aero-engine oils, rapid cooling of these oil solutions of wax was found to give a high viscosity, but it was not found possible to produce, by storage of the blends at room temperature, the progressive increases observed for the gasoline–oil blends.

When solid wax was present in these solutions it was noted that the viscosity of the oil decreased with each successive determination and appeared to approach a constant value after a number of determinations. As mentioned earlier, similar results were obtained with gasoline–oil blends. Some typical results are given in Table VI.

TABLE VI.

Fall in Viscosity with Successive Measurements.

Oil.	Temperature, ° C.	Determination no.	Viscosity, stokes.
Oil A + 20% vol 100-octane fuel	−30	1	61·55
		2	57·27
		3	54·55
		4	53·54
		5	51·91
Medicinal Oil + 0·25% wt wax	0	1	20·10
		2	17·54
		3	16·17
		4	15·82
		5	15·00
Medicinal Oil + 0·25% wt wax	−10	1	58·80
		2	56·30
		3	53·40
		4	52·70
Medicinal Oil + 1% wt wax	0	1	20·09
		2	17·60
		3	15·80
		4	15·40

The reason for these results is not clear, but it is probable that during the flow through the viscometer the aggregates of wax crystals, which have grown during cooling, are broken up so that they offer less resistance to flow, and hence the measured viscosity decreases with successive determinations.

SECTION II. DENSITY OF AERO-ENGINE OILS AT LOW TEMPERATURES.

Since the method used for the measurement of viscosity of a liquid at various rates of shear gives the viscosity in absolute units, it was necessary to carry out density measurements upon these oils at low temperatures in order that comparison could be made with earlier results in kinematic units.

EXPERIMENTAL DETAILS.

Since it is difficult to measure the density of a liquid at low temperatures by the more conventional methods, a type of pyknometer was devised which enabled density measurements to be carried out to an accuracy of

better than 1 per cent at low temperatures. Fig. 6 gives a diagram of the pyknometer when filled. Bulb A has a volume of about 70 ml, and tube D is calibrated so that the volume may be read to $\pm 0{\cdot}01$ ml.

In order to fill the pyknometer, tap B was cut off at the point C, and 20 to 30 ml of mercury, sufficient to fill the lower capillary tubes and the base of the bulb, was weighed into the pyknometer. About 50 ml of oil was then poured into bulb A at C, until A was filled up to the shoulder of the bulb, care being taken not to allow oil to wet the entrance of the bulb at C. Tap B was then re-joined on to bulb A at C. Further weighed quantities of mercury were now poured down tube D until the oil-level reached tap B, care being taken to avoid trapping air bubbles in the

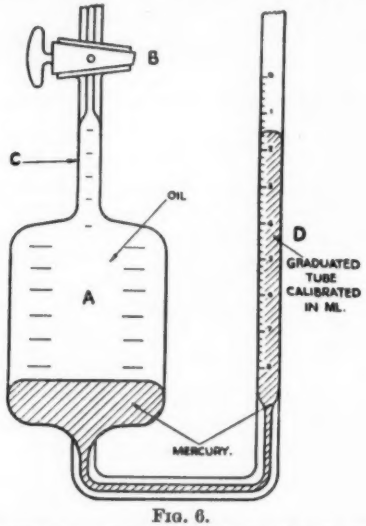

FIG. 6.
PYKNOMETER FOR DENSITY MEASUREMENTS AT LOW TEMPERATURES.

capillary portion of the tube. Tap B was then closed and further mercury added until the mercury level in tube D was at a suitable height. The oil was then enclosed under a pressure of several centimetres of mercury.

The vessel was now placed in a thermostat at 25° C and allowed to attain equilibrium. The reading of the mercury level in tube D was recorded. The pyknometer was then placed in turn in a series of baths maintained at temperatures at which density measurements were required; the thermostatting arrangement used for viscosity measurements was also used for low-temperature density measurements. The pyknometer was left at each temperature for about half an hour to attain uniform temperature and the new mercury level was noted.

When this had been completed the pyknometer was emptied, cleaned, and then completely filled with a weighed quantity of mercury. The pyknometer was then placed in the thermostat at 25° C, and the mercury level in D adjusted to be almost the same as it was when bulb A was filled

with oil. When uniformity of temperature had been obtained the new reading was recorded.

From the two measurements at 25° C and the weights of mercury used, the volume of oil used was easily calculated. The density of the oil at 25° C was measured by the density-bottle method, and hence the weight of oil used could be calculated.

From the International Critical Tables, the density of mercury at temperatures between −38° and +25° C was obtained. Thus, from the measurements taken, if the expansion coefficient of the vessel is known, the contraction of the oil at various temperatures and hence its density can be calculated.

To determine the coefficient of expansion of the vessel, the pyknometer was filled with mercury and a series of measurements of the mercury level at various temperatures similar to those carried out with the oil were recorded. From the apparent volume of the mercury and its true volume (deduced from International Critical Tables density values), the coefficient of expansion of the vessel was calculated. For a given vessel this need only be done once for measurements upon a series of oils.

From these measurements, the density of the oils was calculated. The weighings were carried out to ±0·01 g, and so the accuracy of the density determination was limited by the accuracy to which the graduated arm D could be read (±0·01 ml). The maximum probable error in the density determinations is thought to be 0·0004, but in most cases it is probably less than this.

For the purpose of converting viscosity measurements in stokes to the corresponding value in poises, it was not necessary to calculate densities to such a degree of accuracy, but rough calculations made it evident that useful information concerning the state of the oil could be obtained from its coefficient of expansion, and for this reason more elaborate calculations were made.

TABLE VII.

Density of DTD.472B Oils and Gasoline–Oil Blends at Low Temperatures.

Temp. ° C.	Density, g/ml.					
	Oil A.	A + 10% vol 100-octane fuel.	A + 20% vol 100-octane fuel.	A + 30% vol 100-octane fuel.	Oil C.	Oil B.
25	0·8836	0·8681	0·8522	0·8367	0·8821	0·8773
20	0·8866	0·8712	0·8555	0·8400	0·8851	0·8804
15	0·8897	0·8743	0·8588	0·8433	0·8880	0·8834
10	0·8927	0·8774	0·8621	0·8468	0·8910	0·8865
5	0·8957	0·8805	0·8654	0·8503	0·8940	0·8896
0	0·8987	0·8837	0·8687	0·8538	0·8970	0·8928
− 5	0·9019	0·8869	0·8720	0·8571	0·9001	0·8960
−10	0·9053	0·8901	0·8753	0·8604	0·9032	0·8992
−15	0·9089	0·8937	0·8787	0·8640	0·9063	0·9029
−20	0·9128	0·8977	0·8823	0·8677	0·9104	0·9069
−25	0·9173	0·9016	0·8860	0·8714	0·9148	0·9109
−30	0·9213	0·9058	0·8900	0·8753	0·9191	0·9149
−35	0·9252	0·9096	0·8942	0·8790	0·9224	0·9189

Experimental Results.

The results of the density measurements are given in Table VII, while in Fig. 7 some of the results are shown graphically. It is seen that between about 0° and 60° C the density varies linearly with the temperature, but at temperatures below 0° C the density increases more rapidly. The addition of gasoline to oil A lowers the temperature at which the density ceases to be linearly related to the temperature.

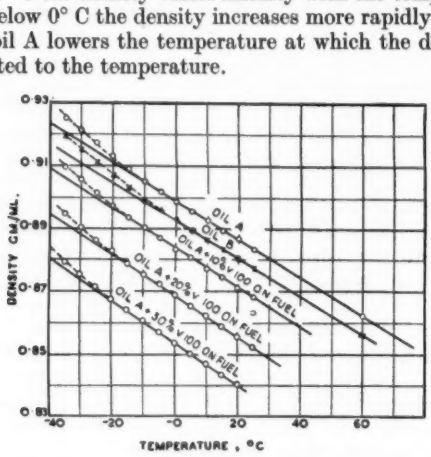

Fig. 7.

DENSITY OF BLENDS OF OIL A AND 100-OCTANE FUEL AND OF OIL B AT LOW TEMPERATURES.

Discussion of Results.

It is seen that, from a temperature a few degrees above the pour point of the oil, the density increases with decreasing temperature at a greater

Table VIII.

Coefficients of Expansion at Low Temperatures.

Temp range, ° C.	Coefficient of expansion of: (per ° C × 10^5).					
	Oil A.	Oil C.	Oil B.	A + 10% vol 100-octane fuel.	A + 20% vol 100-octane fuel.	A + 30% vol 100-octane fuel.
60– 25	70	70	71	—	—	—
25– 20	68	68	71	71	77	79
20– 15	70	66	68	71	78	79
15– 20	68	68	70	71	77	83
10– 5	67	67	70	71	76	83
5– 0	69	67	72	73	76	82
0– 5	71	69	72	73	76	77
−5– −10	75	69	71	72	76	77
−10– −15	80	69	82	81	78	84
−15– −20	86	90	89	90	82	86
−20– −25	99	97	88	87	84	85
−25– −30	87	94	88	93	90	89
−30– −35	85	72	87	84	94	84

rate than that for the temperature range, 60° to 20° C. In Table VIII is recorded the coefficient of expansion of each oil calculated from the density.

Since an error of 0·0001 in the density of the oil at any temperature causes an error of more than 2 per cent in the coefficient of expansion calculated from the density of the oil at a temperature 5° C higher, there are occasionally rather large fluctuations in the coefficient of expansion due to slight errors in density. The results are expressed graphically in Fig. 8 for oils A and C and oil A + 30 per cent 100-octane fuel. It is seen that at temperatures above 0° C, the coefficient of expansion of the oils was constant within experimental error, but below 0° C the coefficient passed through a maximum value.

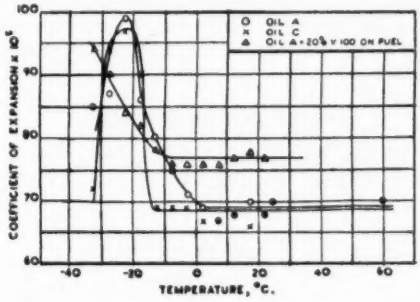

FIG. 8.

INFLUENCE OF TEMPERATURE UPON THE COEFFICIENT OF EXPANSION.

Such a change in the coefficient of expansion is indicative of a change in phase in the liquid, that is to say, it indicates the separation of solid material from the liquid. A similar curve may be obtained by dissolving wax in a wax-free oil; at temperatures above the melting point of the wax, the coefficient of expansion of the solution is practically constant, but on cooling a sudden maximum in the coefficient of expansion–temperature curve coincides with deposition of wax from solution. Similar results have been described by Bondi.[5] From these results it appears that solid hydrocarbons begin to separate from the oils at temperatures below 0° C, and it is significant that these changes occur at the same temperatures as those at which the plot of log T against log log $(\eta + 0{\cdot}6)$ ceases to be linear.

It was also of interest to note that the density was not influenced by the rate of cooling. This implies that the same amount of solid matter is deposited from the oil however rapid the rate of cooling and that any changes in the physical properties of the oils due to different rates of cooling must be ascribed to the state of the deposited material and not to the amount present in the solid state.

It was also noted that if an oil was cooled to a temperature below that at which a density measurement was to be carried out and then allowed to warm up to the desired temperature, its density was usually somewhat greater than the value obtained by direct cooling to that temperature. This was observed only at temperatures below −10° C for oils, and implied that the solid matter, once precipitated from the oil, did not return into

solution for some considerable time, a result which was anticipated from other work.

Section III. Low-temperature Viscosity at Finite Shearing Stresses.

Several series of viscosity measurements on aero-engine oils were made at low temperatures using shearing stresses considerably greater than those in the conventional Ubbelohde viscometer. In the apparatus used, oil is forced upwards through a capillary under air pressures up to 100 p.s.i. In general, it was found that for all temperatures at least 10° C above the A.S.T.M. pour point, aircraft oils behaved as Newtonian liquids for shearing stresses up to 40,000 dynes/sq. cm., while at lower temperatures the apparent viscosity showed a marked dependence upon shearing stress and degree of oil agitation.

Experimental Details.

(i) *Apparatus.* A diagram of the viscometer is given in Fig. 9. It consists of a steel-flanged vessel A and lid B capable of withstanding internal

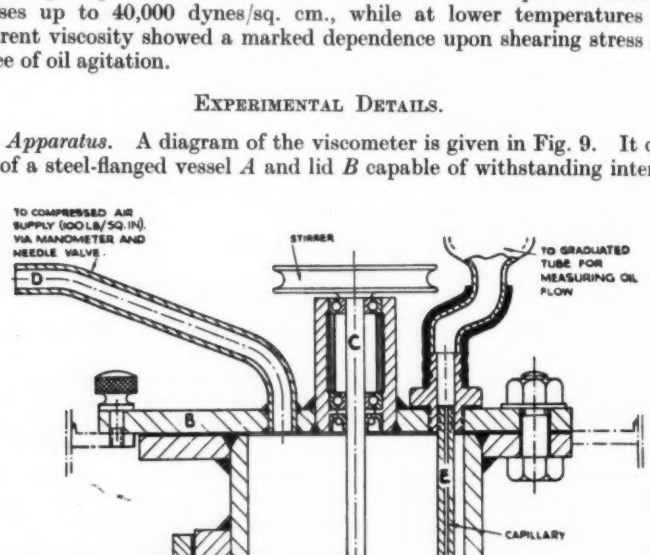

Fig. 9.

DIAGRAM OF THE PRESSURE VISCOMETER.

pressures of over 100 p.s.i. C is a stirrer and seal so arranged that the contents of the vessel may be stirred without leakage of compressed air, which is admitted by tube D. E is a brass capillary up which oil is forced by compressed air and is connected to a graduated tube by means of which the rate of efflux of the oil can be measured. Two thermocouples F and G

are provided in order that the temperature of the oil may be measured, the position of G being such that the oil temperature is measured just before it enters the capillary. The whole vessel is supported in a tank which is connected to the cooling arrangement described earlier in the report. The viscometer is completely submerged in the cooling liquid and may be maintained at any temperature between 20° and −25° C.

(ii) *Test Procedure.* The viscometer was filled with the oil under test to within $\frac{1}{4}$ in of the top and placed in the tank; the cooling-system pump was then switched on and the bath brought to the required temperature. By adjustment of the valves (Fig. 1) it was found possible to maintain the tank temperature constant to within ±0·1° C of any temperature between 20° and −25° C. After cooling for about half an hour, the temperature of the oil around the thermocouples became equal to that of the bath, but to ensure uniform temperature throughout the oil in the viscometer, the apparatus was allowed to stand for a further $\frac{1}{4}$ hr before measurements were begun. At temperatures of −15° C and below, this period was lengthened to 1 hr before commencing measurements. On account of the low conductivity of the oil, it was found that despite fluctuations in the bath temperature, the temperature of the oil as recorded by the thermocouples remained constant to within less than ±0·05° C.

When the cooling period was complete, the compressed-air supply was turned on and, by means of a needle valve and a controlled leak, the pressure in the viscometer was maintained constant at any desired pressure between 10 and 500 cm Hg to within ±1 per cent. The actual pressure was measured on a mercury manometer for pressure up to 125 cm Hg and on a Budenberg gauge, previously calibrated against a standard gauge, for pressures between 125 and 500 cm Hg.

The pressure inside the viscometer forced oil up the capillary, and the rate at which it filled the graduated tube was measured. In order to keep the rate of flow within measurable limits for widely different viscosities, two interchangeable brass capillaries were made, one of diameter 0·046 in and length 3 in, for use at temperatures between 20° and −5° C, for DTD.472 oils, and the other of diameter 0·078 in and length 3 in, for use at lower temperatures. The tubing through which the oil passed after leaving the capillary was about 1 cm diameter and, except for 2 or 3 cm of its length, was in contact with air at atmospheric temperature; hence, the resistance to flow of this tube was negligible compared with that of the capillary.

The rate of flow of the oil into the graduated tube was determined by measuring either the volume of oil flowing up the tube in a period of about 2 min or the time taken for 1 ml to flow through the capillary.

When the rate of flow E through a capillary of length L and radius a at a pressure difference of P across the capillary is known, then the viscosity η can be calculated using the well-known Poiseuille equation

$$\eta = \frac{\pi P a^4}{8EL} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

However, in view of the difficulty in measuring accurately the dimensions of the capillary and the uncertainty introduced by end effects, it was decided to calibrate the viscometer using a liquid of known viscosity.

Calibration of the Viscometer.

Preliminary experiments were carried out at 20° C with oil A in the viscometer. When the rate of flow was plotted against the pressure difference across the capillary, a straight line resulted (Fig. 10). This showed that at 20° C the oil had a constant viscosity over the range of shearing stresses and rates of shear employed, and hence the oil could be considered as a Newtonian liquid at this temperature. Accordingly the viscosity of oil A

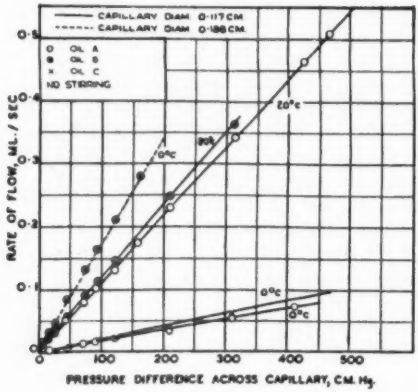

Fig. 10.

Flow–pressure relations in pressure viscometer at 20° and 0° C.

at 20° C, measured in an Ubbelohde viscometer, was taken as the viscosity of the oil in the pressure viscometer. From this value and the plot of rate of flow against pressure, a viscometer constant K embodying the dimensions of the capillary was evaluated and used to calculate viscosities when measurements were made at other temperatures. It can be seen from equation (2) that for a given capillary

$$K = \frac{\pi a^4}{8L},$$

and so

$$\eta = K \cdot \frac{P}{E}$$

In this way errors due to end effects at the entrance and exit of the capillary were eliminated.

Using the narrow capillary at 0° C with oil A, a straight-line plot of pressure difference across the capillary against rate of flow again resulted; the wider capillary was therefore calibrated at 0° C in the same way as the narrower one was calibrated at 20° C. It was found impracticable to calibrate the wider capillary at 20° C owing to the high flow rates obtained.

Using these two capillaries the behaviour of the several oils was investigated at temperatures down to −25° C. In the calculation of these results

a small correction was made to the pressures as recorded on the manometer or gauge to allow for the head of oil in the graduated tube. No allowance has been made for the change in dimensions of the capillary with temperature, since the errors arising from this are small compared with other experimental errors. The total possible error in the measurement of the viscosity at any given pressure difference across the capillary was considered to be less than ± 3 per cent, and the agreement of the results with each other and with Ubbelohde measurements, when the liquid under examination was behaving as a Newtonian liquid, confirmed this.

Experimental Results.

(a) *DTD.472B Oils.* The viscometer was used to measure the viscosities of oils A, B, and C, all DTD.472B oils, at temperatures between 20° and

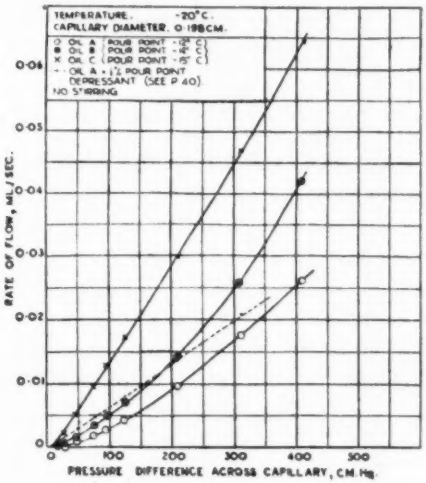

Fig. 11.

FLOW–PRESSURE RELATIONS FOR DTD.472B OILS AT −20° C.

−25° C. As long as the oil was at least 10° C above its pour point, it was found that the relation between rate of flow and pressure difference across the capillary was linear, within experimental error, over the range of shearing stresses investigated; Fig. 10 shows typical curves obtained at 20° and 0° C.

At temperatures of about 5° C above the pour point, these plots became slightly curved, being convex towards the pressure axis. As the temperature was lowered, the curvature of these graphs became more pronounced. Fig. 11 shows typical curves obtained at −20° C. It is evident that at this temperature the laws of Newtonian flow cease to hold good, and the measured viscosity becomes dependent upon the shearing stress. Under these conditions the Poiseuille formula ceases to give the true viscosity of

the oil, but it can be used (as explained previously) to give the apparent viscosity. Figs. 12 and 13 show how the apparent viscosity changes with pressure difference across the capillary at −5°, −10°, and −20° C. It is

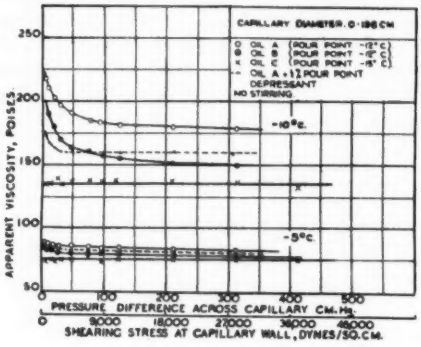

FIG. 12.

APPARENT VISCOSITY *V.* SHEARING STRESS AT CAPILLARY WALL FOR DTD.472B OILS AT −5° AND −10° C.

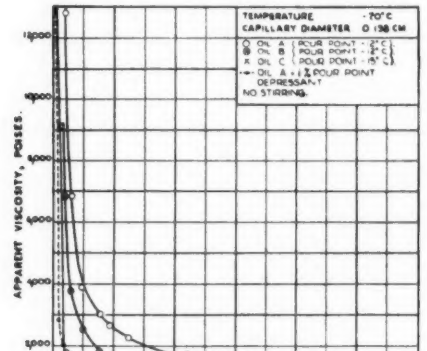

FIG. 13.

APPARENT VISCOSITY *V.* SHEARING STRESS AT CAPILLARY WALL FOR DTD.472B OILS AT −20° C.

seen that even at −20° C oil C, which has the lowest pour point (−15° C) of the three oils, departs from Newtonian behaviour only at shearing stresses below about 5000 dynes/sq. cm. At −25° C, however, as can be seen from Fig. 14, the departure becomes considerable at shearing stresses of less than 9000 dynes/sq. cm.

The results for these oils are tabulated in Table IX; in this table the apparent viscosity of the oil is listed for a series of pressure differences across the capillary at any one temperature. Since the viscosity of different oils was not measured at exactly the same pressure difference at any given temperature, the values given in the table are values obtained at a pressure difference of within ± 10 per cent of the stated value.

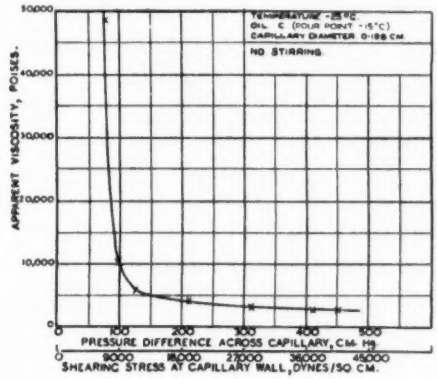

FIG. 14.

APPARENT VISCOSITY *V.* SHEARING STRESS AT CAPILLARY WALL AT −25° C.

(b) *Blends of* 100-*octane Fuel and Oil A.* A blend of oil A containing 10 per cent by volume of 100-octane fuel gave results similar to those for the above oils. At temperatures of more than 10° C above the pour point (−23° C) the blend possessed Newtonian characteristics, but at a lower temperature it showed departures from Newtonian behaviour, the extent of the departures increasing with decreasing temperature. The results are summarized in Table X. It was found impracticable to carry out measurements upon blends containing more than 10 per cent gasoline, owing to the difficulty in maintaining temperatures lower than −30° C with the apparatus used. However, blends with a higher gasoline content would have undoubtedly given behaviour similar to that of the 10 per cent blend, except that the non-Newtonian properties would have developed at lower temperatures.

(c) *Influence of Stirring upon Apparent Viscosity.* The viscometer was fitted with a stirrer designed so that, when stirring was taking place, the oil was subjected to a considerable shearing action just before it entered the capillary. Several experiments were carried out while stirring at a constant speed.

With oil A, at temperatures when the oil was behaving as a Newtonian liquid, the viscosity was found to be the same with and without the stirrer in operation at all pressures up to 300 cm Hg. This shows that the stirrer does not give rise to any turbulent effects which interfere with streamline flow through the capillary.

At temperatures at which the oil showed departures from Newtonian

TABLE IX.

Comparison of Ubbelohde Viscometer with Pressure Viscometer Data.

Temp, ° C.	Ubbelohde viscosity, poises.	Apparent viscosity (poises) of oil at pressure difference across capillary of: (cm Hg).						Viscosity extrapolated from A.S.T.M. chart, poises.
		10.	50.	100.	200.	300.	400.	
		Oil A (A.S.T.M. pour point −12° C).						
20	7·87	Constant—used for calibration						—
10	18·96	Constant at all pressures 18·1 ± 0·3 poises						18·3
0	50·15	Constant—used for calibration						50·3
− 5	88·7	86·9	95·2	84·0	83·0	82·5	—	81·2
−10	217	210	192	184	181	178	—	154
−15	1772	950	640	550	480	440	410	300
−20	No flow	(20 cm Hg 12,800)	3800	2500	1750	1400	1250	630
		Oil B (A.S.T.M. pour point −12° C).						
20	7·61	Constant at all pressures 7·4 ± 0·2 poises						—
10	17·53	Constant at all pressures 17·4 ± 0·3 poises						17·7
0	49·4	47·0	45·3	44·6	44·4	44·2	43·8	45·5
− 5	95·5	83·0	79·2	78·3	77·7	—	—	78·0
−10	202	190	163	155	153	—	—	152
−15	1460	640	430	380	330	310	300	298
−20	No flow	(20 cm Hg 6740)	2500	1500	1100	900	780	617
		Oil C (A.S.T.M. pour point −15° C).						
20	7·80	Constant at all pressures 7·7 ± 0·2 poises						—
10	17·85	Constant at all pressures 17·6 ± 0·5 poises						17·8
0	47·1	Constant at all pressures 44·0 ± 2·0 poises						46·6
− 5	81	Constant at all pressures 74·6 ± 0·6 poises						80·1
−10	143	Constant at all pressures 136 ± 2 poises						140
−15	309	270	265	262	260	258	257	263
−20	No flow	9100	760	590	540	510	490	502
−25	No flow	No flow	385,000	10,000	4100	3000	2900	1372

TABLE X.

Viscosity of Oil A + 10% vol 100-Octane Fuel in Ubbelohde and Pressure Viscometers.

Temp, ° C.	Ubbelohde viscosity, poises.	Apparent viscosity (poises) of blend at pressure difference across capillary of: (cm Hg).						Viscosity extrapolated from A.S.T.M. chart, poises.
		10.	50.	100.	200.	300.	400.	
10	3·74	3·74	3·75	3·75	—	—	—	3·74
0	8·09	8·06	8·01	7·98	—	—	—	8·39
−10	20·18	20·1	20·3	19·9	20·3	20·3	—	20·0
−15	37·54	37·1	34·5	34·4	34·6	33·8	34·0	33·0
−20	117·8	112·0	91·8	89·3	86·9	81·5	80·8	56·6
−25	3570	696	318	275	233	222	212	108
−30	No flow	*	2910	1510	1020	802	763	190

* No flow at 10 cm Hg; 20 cm Hg, 368,000.

behaviour, the operation of the stirrer had considerable influence upon the apparent viscosity. Fig. 15 shows some typical flow–pressure curves obtained with oil A at −20° C with the stirrer operating at various speeds. It is seen that, at least initially, the flow–pressure curve became linear

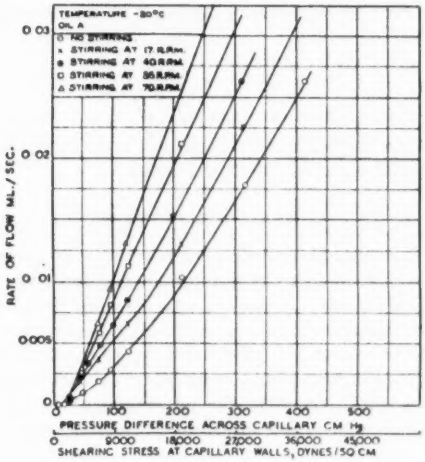

FIG. 15.

INFLUENCE OF STIRRING UPON APPARENT VISCOSITY.

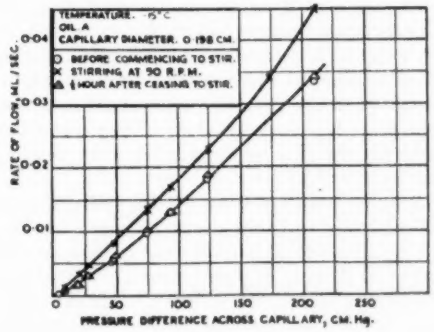

FIG. 16.

FLOW–PRESSURE CURVES WITH AND WITHOUT STIRRING.

within experimental error, but did not pass through the origin. At higher pressures this linear relationship appeared to break down and the curve became approximately parallel to the curve for the unstirred oil. The greater the rate of stirring, the steeper was the gradient of the linear portion of the flow–pressure curve and the higher was the pressure difference across the capillary before the line showed curvature. Similar results have been

obtained for all the oils and blends investigated. It is obvious from these graphs that the lowest apparent viscosities at any given pressure are obtained when the stirring rate is greatest.

This phenomenon was found to be quite reversible, for on ceasing to stir and allowing to stand for about ¼ hr, the flow–pressure curve obtained was identical with that obtained before stirring. This is illustrated in Fig. 16 for oil A at −15° C.

Discussion of Results.

From the previous results it is seen that at a temperature of about 10° C above the pour point, several marked changes occur in the properties of the oils. Firstly, the oils cease to obey the relation

$$\log T = k \log \log (\eta + 0{\cdot}6) + c \quad . \quad . \quad . \quad . \quad (1)$$

secondly, the coefficients of expansion commence to increase suddenly, and thirdly, the oils cease to behave as Newtonian liquids. Further, it appears that solid hydrocarbons commence to separate out from the oils at this temperature, and it is reasonable to suppose that it is this phase change which causes the changes in the physical properties of the oils.

The change in flow characteristics of an oil can be satisfactorily explained by the presence of solid matter in the oil; in fact, it is with suspensions of solids in liquids and colloidal solutions that anomalous flow characteristics are found.

When solid matter is present in the liquid, the solid particles or crystals can interlock or interfere with streamline flow and thereby increase the viscosity of the liquid. Increased shearing stresses break down the interlocking of particles and give rise to a greater degree of orientation of the particles; in this way the resistance to flow is decreased. At high shearing stresses, the stresses are so great that any tendency of the solid to interlock is overcome and orientation of the particles for easiest flow becomes complete, with the result that the viscosity of the fluid approaches that of the liquid in which the particles are suspended. The greater the concentration of solid matter, the greater will be the tendency for the particles to interlock and so the greater will be the viscosity.

Increasing the concentration of solid matter will eventually give rise to a degree of interlocking so great that it may impart a kind of rigidity to the liquid, as exists in gel structures, so that at low shearing stresses the liquid will not flow but will possess a yield value. As the shearing stress is increased, it will eventually become sufficiently great to break the weaker links in the lattice of solid particles and flow will commence.

In the case of oils, at temperatures well above the pour point, there will be no solid matter present and flow will occur according to the normal Newtonian laws. On cooling, as the pour point is approached, solid hydrocarbons will crystallize out and offer resistance to flow giving rise to a viscosity greater than that predicted by equation (1). These crystals, at very low rates of shear, will have a random orientation and will interlock with other crystals giving a lattice-like structure. The greater the rate of cooling, the smaller is the crystal size and the greater the degree of interlocking. As the rate of shear is increased, these crystal lattices will be

more and more completely broken down, the individual groups of crystals will be orientated so that they offer less and less resistance to flow, and the apparent viscosity will decrease. As the temperature is decreased below the pour point, more solid will separate out and so the viscosity will rapidly become much greater than its predicted value and it will also become more and more dependent on the rate of shear. In the limit, at very high rates of shear, the crystal aggregates will be completely broken down into single crystals and will be completely orientated so that the viscosity should become constant once again.

The results obtained fit into this general picture, for at each temperature the viscosity decreases to a limiting value as the shearing stress is increased. This limiting value must be nearly equal to the viscosity of the oil in which the solid hydrocarbons are suspended. Now equation (1) predicts the viscosity of the oil assuming no phase separation has occurred, and so, provided that the amount of solid matter is small and/or its removal does not markedly change the viscosity of oil at temperatures when Newtonian flow occurs, then one would expect that at high rates of shear the apparent viscosity would be almost equal to the predicted viscosity. Examination of the results shows that this is the case to within a few per cent at temperatures above about $-15°$ C. Below this point, the apparent viscosity at the highest shearing stress employed is considerably greater than the predicted viscosity. However, at these temperatures the apparent viscosity is still decreasing appreciably with shearing stress at an appreciable rate and so even at higher shearing stresses the apparent viscosity will undoubtedly approach more nearly the predicted value.

Examination of the results and the flow–pressure curves with and without stirring indicates that these oils may possess a small yield value. With oils A and B at $-20°$ C and C at $-25°$ C, it was not possible to detect any flow over a period of $\frac{1}{4}$ hr at shearing stresses of less than 800 dynes/sq. cm. at the walls of the capillary (about 10 cm Hg pressure difference across the capillary). It would appear therefore that these oils behave as plastic materials at low temperatures.

(d) *Slip.* To ensure that slip was not giving rise to erroneous values for the apparent viscosity, some experiments were carried out using the narrow capillary at low temperatures. It has been shown by Mooney [7] that, if slip is absent and the viscosity of the material is simply a function of the shearing stress, the curves obtained by plotting $\frac{E}{\pi a^3}$ against S_a will be coincident for all capillaries. For the three oils investigated, it was found that down to temperatures of $-15°$ C the curves obtained with the two capillaries were, within experimental error, coincident. At $-20°$ C the two curves were separated by an amount which was thought to be rather greater than experimental error. As shown in Section III (*f*) the rate of cooling from 60° C can have a profound influence upon the viscosity of a waxy raffinate measured at room temperature, and since the above experiments with different capillaries were carried out on different days, it is possible that the lack of coincidence of the two $\frac{E}{\pi a^3}\Big|S_a$ curves may be due to slight differences in cooling rates. Hence, it appears that no slip occurred when measurements were made at temperatures of $-15°$ C and

above, but at −20° C and below, it is possible that some slip may have occurred.

(e) *Thixotropy.* The experiments carried out with the stirrer in operation showed that these oils are thixotropic at low temperatures. Preliminary experiments showed that the structure in the oil is not broken down immediately a shearing stress is applied to it. The viscometer containing oil A was cooled to −15° C and a constant pressure applied to the oil. The rate of flow of the oil was such that the contents of the capillary were renewed several times a minute, and measurements showed this rate of flow to be constant. The stirrer was then set in motion at about 50 r.p.m. and the rate of flow of the oil increased, but it was not until some 15 min had elapsed that the flow rate again became constant. The rate of increase of the flow was greatest immediately on starting the stirrer and it then gradually decreased to zero. When stirring was discontinued, a similar change in the flow rate occurred, and about 15 min after stirring ceased the flow had decreased the original value.

This rough experiment showed that the extent of break-down and build-up of structure in the oil was dependent upon the time for which the shearing stress had been acting upon the oil and that the oil showed a considerable degree of thixotropy.

As a tentative explanation of the results obtained at various rates of stirring it is suggested that when the oil is stirred at a constant rate its structure is partly broken down. On applying pressure to the viscometer the oil is forced into the capillary. Initially at low shearing stresses, the shearing stress acting in the capillary will be less than that imposed on the oil by the stirrer. That is, the degree of breakdown of structure in the oil entering the capillary is greater than that which could be imposed by the shearing stress acting in the capillary alone and so, for that particular stress acting in the capillary, the structure has been completely broken down and all the energy will be utilized in causing flow of the oil. This state of affairs will persist as the pressure across the capillary is increased until the maximum shearing stress in the capillary equals that induced by the stirrer. It is reasonable to assume that when the oil is flowing under a shearing stress and its structure has previously been broken down to an extent greater than that which this shearing stress could produce, then the rate of flow increases linearly with the shearing stress. Results leading to a similar conclusion have been obtained for oils and suspensions of pigments in oils by Green and co-workers [3] using a torsional viscometer. Any further increase in the pressure difference across the capillary will lead to shearing stresses in the capillary greater than those caused by the stirrer, and so further structural breakdown in the capillary must occur. The flow–pressure curve will then cease to be linear and is similar in type to that obtained for the unstirred oil, but since some of the structure of the oil has been broken down before entering the capillary, the stirred oil offers less resistance to flow than the unstirred oil, with the result that its apparent viscosity is less than that of the unstirred oil flowing under the same shearing stress.

These experiments were all carried out at −15° C or below, in which range the difficulty of maintaining constant temperatures for long periods of time may result in an appreciable experimental error. In an attempt to

gain more accurate information about the behaviour of these oils at low temperatures, the behaviour of some waxy raffinate blends which appeared to give similar results at higher temperatures was investigated, and is discussed below. Unfortunately, owing to time considerations, it was possible only to show that the behaviour of these waxy blends at about 20° C was rather similar to one of the DTD.472B oils at about −20° C. Hence, it is not at present possible to substantiate entirely the above suggestions concerning the behaviour of oils at low temperatures.

(f) *Viscosity of Oils Blended from a Waxy Raffinate.* In an attempt to obtain an oil which showed anomalous viscosity at or about room temperature, several experiments were made using blends containing a waxy raffinate. This raffinate, which when dewaxed constituted the heavy component of oil B, contained about 30 per cent wax which is normally removed by dewaxing at −20° F in the refinery dewaxing plant. While these experiments did not quite achieve their main object, it is considered that the results are of sufficient interest to be recorded in this paper.

Three blends were made up by mixing the waxy raffinate with a small proportion of a light solvent-extracted oil * and oil B in such a way that at 60° C, the temperature at which the wax in the raffinate dissolved completely, the viscosity of each was approximately the same as that of a DTD.472B oil. The composition of the blends is given in Table XI. The

TABLE XI.

Composition of Blends Containing a Waxy Raffinate.

Component.	Composition, % wt.		
	Blend 1.	Blend 2.	Blend 3.
Waxy raffinate	14·0	23·3	35·0
Light solvent extracted oil * . .	6·0	10·0	15·0
Oil B	80·0	66·7	50·0

* This oil had a viscosity of about 340 cs at 15° C.

blends were made up by heating the mixtures of the three components to 60° C and then allowing them to cool slowly in an oven at a rate of about 10° C per hour. At room temperature, microscopic examination of these blends showed that all contained solid wax in suspension. Viscosity measurements using the pressure viscometer at 20° C showed that this wax gave rise to a viscosity which was only slightly dependent upon the shearing stress. Fig. 17 shows the relation obtained at 20° C between the apparent viscosity and the shearing stress at the capillary wall, and it will be seen that the dependence of viscosity upon shearing stress increased with increasing wax content, though even with Blend 3 the apparent viscosity is only about 60 per cent greater at 900 dynes/sq. cm. than it is at 30,000 dynes/sq. cm.

Although it was hoped that the viscosity of these blends at 20° C would depend on shearing stress in the manner observed at −20° C with oil B, no

* This oil had a viscosity of about 340 cs at 15° C.

such effect occurred above a temperature of −15° C. Even at −20° C, despite the additional presence of about 5 per cent wax, it was found that the behaviour of Blend 1 was not markedly different from that of oil B.

These results suggest that it is the joint effect of the solid hydrocarbons separating out at low temperatures and the high viscosity of the suspending medium which is mainly responsible for the controlling influence of shearing stress on viscosity. Owing to time considerations, this point was not investigated further. It has since been noticed that Zherdeva and co-workers [9] have expressed the view that anomalous viscosity effects which they have obtained with " wax-free oils " result from changes which occur in the basic properties of the hydrocarbon molecules. They consider a " pseudo-crystallization " to take place which destroys the fluidity of the

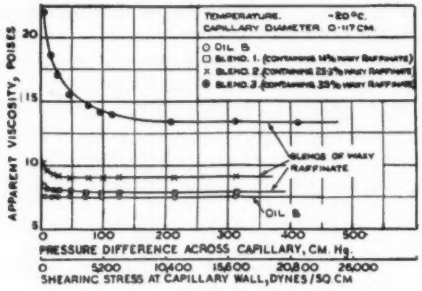

FIG. 17.

APPARENT VISCOSITY *v.* SHEARING STRESS FOR OILS CONTAINING WAXY RAFFINATE.

oil, presumably without the separation of a solid phase, since they failed to obtain any solid matter by low-temperature filtration.

A few experiments were also carried out using undiluted waxy raffinate alone in the pressure viscometer. Two samples of the raffinate were taken and warmed to 60° C. One of them was allowed to cool slowly in an oven, while the other was cooled to 20° C as rapidly as possible. Microscopic examination of the two samples in polarized light showed that the rapidly cooled sample consisted of a suspension of very minute needle-like wax crystals, while the slowly cooled sample contained comparatively large and more lamellar crystals. The viscosity of each of the two samples was measured at 20° C in the pressure viscometer up to as high a pressure as was possible. It was found that, at a pressure difference of about 250 cm Hg across the capillary, " channelling " occurred owing to the high viscosity of the oils at low shearing stresses. The rate-of-flow–pressure-difference curves are shown in Fig. 18; it is seen that the rapidly cooled sample containing a large number of small wax crystals had a very much higher apparent viscosity especially at low shearing stresses than did the slowly cooled sample containing relatively large crystals. With this latter sample, it was also possible to carry out measurements with the stirrer in operation at 100 r.p.m. when the results obtained were very similar to those obtained with oil A at −20° C (Fig. 15).

These results made it evident that to obtain anomalous viscosity

behaviour in an oil at room temperature comparable with that obtained with DTD.472B oils at −20° C, a considerable amount of solid material must be present. Whether the same amount of solid material is present in DTD.472B oils at −20° C is doubtful. The experiments also showed that the crystal size of the suspended matter can have a considerable

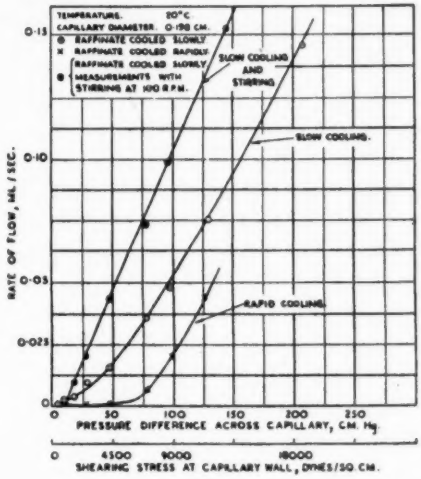

FIG. 18.

FLOW–PRESSURE CURVES FOR THE WAXY RAFFINATE.

influence upon the flow of characteristics and that small crystals are more conducive to anomalous behaviour than large. The importance of the thermal pre-treatment is also brought out.

SECTION IV. THE VISCOSITY OF OILS CONTAINING A POUR-POINT DEPRESSANT.

In order to lower the pour point of an oil it has become customary during the past few years to add a pour-point depressant. Some experiments were therefore carried out to investigate the influence of such an additive upon the viscosity of an oil at low temperatures.

(a) *Ubbelohde Viscosity Measurements.* Measurements were carried out upon oil A + 0·5 per cent pour-point depressant and upon a blend consisting of 14 per cent waxy raffinate, 6 per cent light solvent-extracted oil, and 80 per cent oil B + 1 per cent pour-point depressant. This latter blend was chosen since it had the same viscosity at high temperatures (>60° C) as oil A. The results are given in Table XII, together with the viscosities of the same oils without the additive for comparison.

In Fig. 2 the dotted curve represents the results for oil A + 0·5 per cent pour-point depressant, while Fig. 19 shows the ratio η/η', of the apparent to the predicted viscosity plotted against temperature. Both curves illustrate the deviation observed from equation (1).

TABLE XII.

Influence of the Pour-point Depressant on Ubbelohde Viscosities.

Temp, ° C.	Kinematic viscosity, stokes.			
	Oil A.	Oil A + 0·5% pour-point depressant.	14% Waxy raff, 6% light solvent-extracted oil, 80% oil B.	14% Waxy raff, 6% light solvent-extracted oil, 80% oil B + 1% pour-point depressant.
60	0·882	—	0·818	0·821
20	8·88	8·88	9·64	8·98
15	—	—	16·0	14·0
10	20·12	20·45	27·5	23·1
5	—	—	49·5	37·5
0	55·8	54·2	118·8	67·3
− 5	98·3	95·0	Flow very slow	137·0
−10	240·0	184·6	—	—
−15	1950	1458	—	—
A.S.T.M. pour-point, ° C.	−12	−17	−4	−10

It is seen that the presence of the pour-point depressant extends towards lower temperatures the range in which the above relation holds. For this

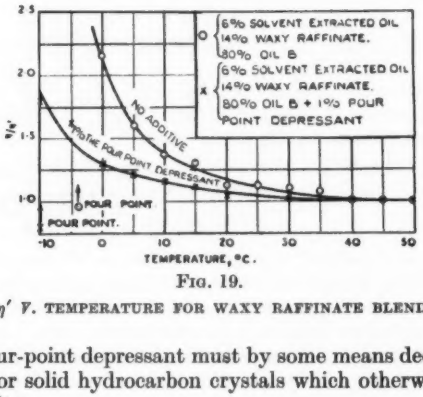

FIG. 19.

η/η' *V.* TEMPERATURE FOR WAXY RAFFINATE BLENDS.

to occur, the pour-point depressant must by some means decrease the interlocking of wax or solid hydrocarbon crystals which otherwise gives rise to increased viscosity.

(b) *Density Changes on Cooling for Oils Containing a Pour-point Depressant.* By the method described earlier in Section II the density of the above oils was determined at temperatures between −25° and 60° C. The results are shown graphically in Fig. 20; it is obvious from the figure that the addition of the pour-point depressant has no significant influence upon the change of density (that is, coefficient of expansion) of the oils with temperature. This implies that the pour-point depressant in no way changes the amount of solid hydrocarbon separating from a given oil at a given temperature, so

that the pour-point depressing action cannot be due to solid hydrocarbons being retained in solution in the oil by the pour-point depressant. Microscopic examination of wax crystals deposited from the waxy raffinate blend with and without the addition of a pour-point depressant showed no obvious difference in shape or size provided the rate of cooling was the same for both blends. The presence of a pour-point depressant has therefore no apparent influence upon crystal formation, and its pour-point depressant action must be ascribed to some other mechanism.

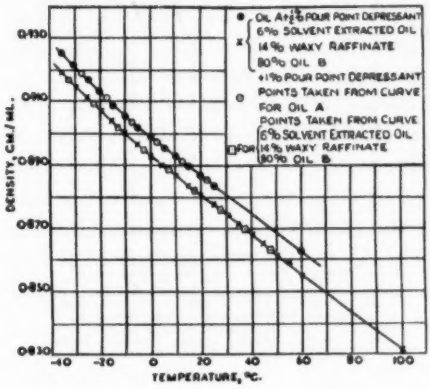

FIG. 20.

INFLUENCE OF POUR-POINT DEPRESSANT ON DENSITY OF OILS AT LOW TEMPERATURES.

(c) *Pressure Viscometer.* Measurements, similar to those made in the case of oil A under high shearing stresses in the pressure viscometer, were carried out upon oil A + 0·5 per cent pour-point depressant. The results are shown by the dotted curves in Figs. 11, 12, and 13. It will be seen that the additive markedly suppresses the dependence of viscosity upon shearing stress. Except at low shearing stresses the apparent viscosity–shearing-stress curves are practically horizontal straight lines. It is of interest to note that the viscosities of oil A and oil A + 0·5 per cent pour-point depressant appear to tend to the same limit as the shearing stress is increased. At low shearing stresses the viscosity of oil A + 0·5 per cent pour-point depressant is slightly dependent upon shearing stress, this effect becoming greater as the temperature decreases, but even at the lowest shearing stress applied, its viscosity is many times smaller than that of oil A alone. The results show that the pour-point depressant enables the solid hydrocarbon lattice structures to be broken down more easily by an applied shearing stress.

Pressure-viscometer measurements were also carried out upon the waxy raffinate blend and similar results were obtained; Figs. 21 and 22 show typical results obtained at −20° and −10° C respectively.

(d) *Mode of Action of the Pour-point Depressant.* These results make it clear that the pour-point depressant does not influence the amount of wax or solid hydrocarbon in suspension at any given temperature, nor does it

appear to influence the apparent crystal size. It must therefore act by reducing the rigidity of the crystal lattices and/or by enabling the crystals to slide past each other more easily. The most obvious way in which this

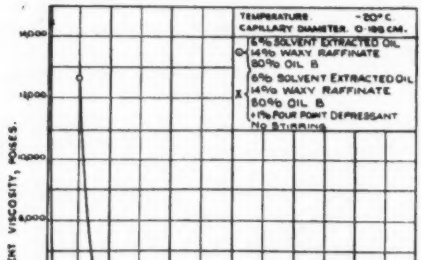

FIG. 21.

INFLUENCE OF POUR-POINT DEPRESSANT UPON APPARENT VISCOSITY.

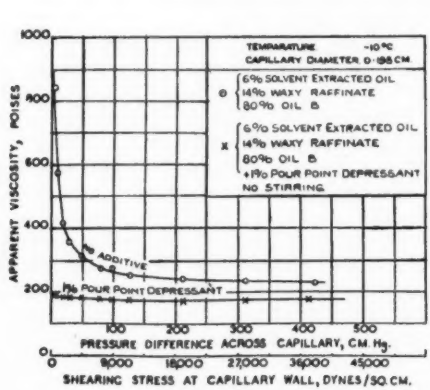

FIG. 22.

INFLUENCE OF POUR-POINT DEPRESSANT UPON APPARENT VISCOSITY.

could occur is by the formation on the hydrocarbon crystals of an adsorbed surface layer of molecules which prevents the interlocking and possibly the actual union of one crystal with another. Similar views on the mode of action of pour-point depressants have been expressed by other workers,[2, 5, 10]

although it has been claimed [2] that the pour-point depressant also influences the crystal size.

Section V. Calculation of the Absolute Viscosity.

As stated earlier, the apparent viscosity of an oil calculated from the flow rate through a capillary tube is not the true viscosity of the oil but is the viscosity of a Newtonian liquid which would flow at the same rate as the oil under the experimental conditions used. The expression $\frac{4E}{\pi a^3}$ only represents the rate of shear at the walls of the capillary when the viscosity of the oil remains constant with variable shearing stress and, generally speaking, does not represent the rate of shear at any point in the capillary for a non-Newtonian liquid. The rate of shear when a liquid is flowing through a capillary may be expressed in its most general form as $\frac{dv}{dr}$, where v is the velocity at a distance r from the axis of the capillary.

Several workers [7, 11, 12, 13, 14, 15] have developed methods of deducing the absolute viscosity of a non-Newtonian fluid from experimental capillary-tube flow data. Of these methods, that evolved by Mooney [7] is the most convenient for the calculation of the absolute viscosity from the present results. In his original paper, Mooney introduced factors taking into account any slip occurring at the capillary walls. Under the experimental conditions, slip appears to be absent at temperatures of $-15°$ C and above, while at $-20°$ C it may occur to a slight extent, but errors arising from its neglect will be slight. By applying Mooney's treatment to the present conditions and neglecting the corrections for slip, the absolute viscosity is given by the equation

$$\frac{1}{\eta_a} = \frac{3}{4} \cdot \frac{1}{\eta_A} + \frac{1}{\pi a^3} \cdot \frac{dE}{dS_a}$$

where η_a = the absolute viscosity at a shearing stress S_a;
η_A = the apparent viscosity when a shearing stress S_a is acting at the capillary wall;
a = radius of the capillary;
E = rate of efflux.

To obtain $\frac{dE}{dS}$, a flow curve was constructed by plotting E against S; tangents drawn to this curve allowed numerical values of $\frac{dE}{dS}$ to be computed, and hence, using the above equation, the absolute viscosity could be determined.

After the viscosity of the fluid has been obtained, the rates of shear involved can then be calculated from the equation

$$S_a = \eta_a \cdot \frac{dv}{dr}$$

In Fig. 23, the calculated absolute viscosity at $-20°$ C for the oils A, B, and C are plotted against the shearing stresses. It is seen that the absolute

viscosity is always less than the apparent viscosity (cf. Figs. 13 and 23), but these approach each other in value at high shearing stresses. At low shearing stresses (less than 1000 dynes/sq. cm.) the apparent viscosity may be several times greater than the absolute viscosity, that is, the apparent viscosity and absolute viscosity differ considerably only when the curvature

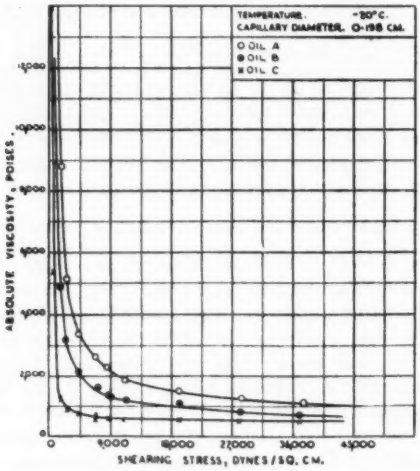

FIG. 23.

VARIATION OF ABSOLUTE VISCOSITY WITH SHEARING STRESS.

of the flow-shearing stress curves is large. It must be borne in mind that, since these oils are thixotropic at −20° C, the values for the absolute viscosity apply only to the specified experimental conditions; the use of a longer capillary of the same radius would involve a greater breakdown of thixotropic structure and so the flow curves obtained would give lower values for the absolute viscosity.

In Fig. 24 the variation of the absolute viscosity with rate of shear is illustrated, while Fig. 25 shows the relation between shearing stress and rate of shear. The absolute viscosity has been calculated for these oils at −20° C only, since at higher temperatures the difference between the absolute and apparent viscosity is only a matter of a few per cent.

No attempt has been made to establish empirical equations for the flow curves, as it is felt that until more is known about the thixotropic behaviour of these oils any such equations would be valueless. It may be said, however, that no simple relationship appears to exist between rate of shear and shearing stress, and, in particular, the empirical equations for the flow curves established by Blott and Samuel [16] for certain greases have no parallel for these lubricating oils at low temperatures, although the shapes of the absolute viscosity, shearing stress, and rate of shear curves are rather similar.

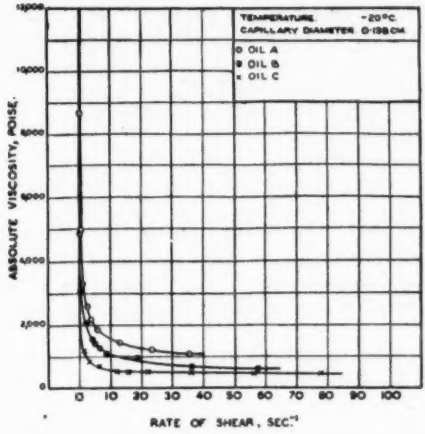

FIG. 24.

VARIATION OF ABSOLUTE VISCOSITY WITH RATE OF SHEAR.

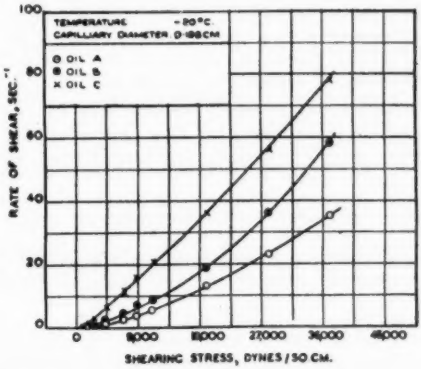

FIG. 25.

RELATION BETWEEN SHEARING STRESS AND RATE OF SHEAR.

GENERAL CONCLUSIONS.

The viscosity measurements carried out in *Ubbelohde viscometers* show that the A.S.T.M. viscosity–temperature chart (*i.e.*, equation (1)) becomes valueless for predicting the viscosity of a lubricating oil conforming to the DTD.472B specification at temperatures near and below the A.S.T.M. pour points. The pour point of an oil gives an indication of the temperature at which the difference between the measured viscosity and the predicted value becomes serious and also roughly determines the temperature at which viscosity becomes dependent on rate of cooling. For an aero-

engine oil diluted with gasoline, the pour point also indicates the temperature at which viscosity becomes dependent upon storage history and mechanical treatment. From the practical standpoint, the viscosity and pour point as normally determined may not give a good indication of viscosity of a diluted oil at low shearing stresses or of an oil cooled suddenly after long storage.

The measurements carried out in the *pressure viscometer* show that at low temperatures, for which the viscosity–temperature chart ceases to be of use, the viscosity of oil and oil–gasoline blends becomes dependent upon the applied shearing stress. The extent to which this occurs is not related to any of the physical properties normally measured for an oil, and although the pour point gives an indication of the temperature at which such effects occur, it does not give any idea of the extent of the departure from Newtonian behaviour.

The viscosity studies, considered in conjunction with the density measurements, show that these anomalous effects are due to the deposition of wax or other solid hydrocarbons from an oil at low temperatures. The magnitude of these effects appears to be related to the crystal size of these solid hydrocarbons and to the quantity present. The crystal size is largely controlled by the rate of cooling, but it has not been possible in this work to establish any quantitative relationship between anomalous effects and the quantity and crystal size of the solid material present.

The measurements carried out upon oils containing a pour-point depressant show that the additive not only depresses the pour point of an oil, but also enables the network of crystals in the oil, assumed responsible for the anomalous behaviour, to be more easily broken down by an applied shearing stress. In other words, it improves the flow characteristics under pressure at low temperatures; this is especially marked at temperatures below the pour point.

Practical Considerations.

For starting aircraft engines at low temperatures, general experience has shown that the important aspects of lubricating-oil performance are as follows :—

(*a*) The oil must be able to flow into the " hotwell " (or " hopper ") in the tank under its own head, and also into the pressure and scavenge pumps under the respective suction head. If the viscosity characteristics of the oil are such that " channelling " takes place, then it is possible that in the first case, the oil may be consumed more rapidly than the oil can flow into the hotwell, while in the second case, the pumps may cease to pump oil, giving rise to failures associated with loss in oil pressure.

(*b*) Frictional forces involved in shearing viscous oil films in bearings, between piston and cylinder wall, in gear-boxes, etc., must all be overcome by the electrical starter. General experience suggests that both the initial starting torque and the subsequent steady rotational drag are of importance in considerations of cold-starting procedure.

From the point of view of assessing the merit of lubricating oils for cold-starting purposes, this paper shows that the ordinary inspection data can

give useful information. Thus, the viscosity at any temperature may be estimated from the A.S.T.M. viscosity–temperature charts or equation (1), and this relationship may be extrapolated down to about 10° C above the A.S.T.M. pour point. The pour point itself represents a rough guide to the temperature at which wax has crystallized out to such an extent that, at low shearing stresses and rates of shear, the viscosity has increased to a value considerably above that obtained by extrapolation from the A.S.T.M. chart. The pour point therefore roughly defines the temperature at which difficulties due to high viscosity under low shear and rates of shear may be expected to arise. For example, channelling in the tank and pump inlet may be expected at temperatures in the neighbourhood of the pour point, and at this temperature the initial starting torque may become very great. Frictional drag once the engine is turning over will be proportional at high shearing stresses to the viscosity which may be roughly estimated from the A.S.T.M. chart by extrapolation. Exact calculation of the viscous drag in the engine is clearly not an easy matter in view of the dependence of viscosity on rate of shear, the shearing stress, and the rate of cooling.

Dilution of an aircraft oil with gasoline achieves a marked lowering in pour point, though the rate of cooling influences the measured viscosity at low shearing stresses down to some 15° C above the measured pour point. However, the addition of gasoline produces a very large drop in the viscosity at low temperatures, and A.S.T.M. chart extrapolations from the 100° and 210° F viscosity values may be possible to temperatures as low as −20° C for 20 per cent 100-octane fuel in oil A and −30° for 30 per cent 100-octane fuel in the same oil.

The addition of a pour-point depressant to aircraft oils lowers both the pour point and the low-temperature viscosity at high and low shearing stresses, and its use in oils in cold climates would be clearly advantageous from the point of view of cold-starting requirements.

The author wishes to express his thanks to the "Shell" Refining and Marketing Company, Ltd., for permission to publish this work, which was carried out in their laboratories.

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Appendix.

Properties of 100-*Octane Fuel.*

Hydrocarbon analysis:	1·5% olefins 12% aromatics 14% naphthenes 72·5% paraffins
Specific gravity 60/60° F:	0·719
Reid vapour pressure:	6·2 p.s.i. at 100° F
Air-free vapour pressure:	179 mm Hg at 20° C
A.S.T.M. distillation:	I.B.P. 43° C 10% at 57° C 50% ,, 91° C 90% ,, 119° C E.P. ,, 164° C
Sulphur:	<0·01%

Discussion.

The President: You will agree that we have a lot to digest in the curves which have been shown. Perhaps we may be reminded that the abnormal pour point of mineral oils was a matter of very serious importance during the war. I remember a paper which was presented to the "Fuels and Lubricants Section" of the S.A.E. about November 1946 describing work which was done by the Standard Oil Development Co. on abnormal pour points, and the thing which struck me particularly was the enormous amount of energy which was needed in investigating this particular subject. An observation post was erected in Canada, and there was a team of observers watching many hundreds of samples of oils. The results have been published. It was the magnitude of the work which impressed me so forcibly.

It is hardly necessary to remind this audience what is meant by dilution of lubricating oils in service with either kerosine or petrol. Kerosine was used many years ago in North America in order to obtain a lower pour point in oils actually in service in trucks. So there is nothing new in that. It was used also during the Russian campaign in the last war, and a certain amount of lubricating oil was diluted with petrol for aircraft engines during the earlier operations; I think it is true to say that during the later part of the campaign it was more usual to add petrol to the lubricating oil when the aircraft landed so that the oil would have a lower pour point, and therefore easier starting at low temperatures. Of course, the petrol evaporated when the engines commenced to run.

You will begin to realize the practical importance of this paper and what Mr Daniel was trying to establish, we hope, once and for all.

The term "pour point" has obviously meant something quite definite; it is the temperature at which oil will pour as distinct from the temperature at which oil will flow. The apparatus which is used for measuring pour point gives a very clear indication of the meaning of the term. Many practical people want to know the temperature at which the oil will pour out of a barrel. Possibly they say that obviously it pours out at the pour point; but obviously it doesn't, because much depends upon the circumstances. I carried out tests some years ago and the results were published in my book "Lubricating and allied oils." The interest-

ing point is that the viscosity of oils at the pour point varies quite a lot. The difference is very much magnified in the presence of fatty oil. You may say that you would expect that because, if rape oil is present, some of the constituents of the rape oil will crystallize. Apparently that was not the case in the samples of which I am speaking, for the oils remained quite clear to the eye.

I had two oils having a pour point at 10° F. One of them was a pure mineral oil, the other some pure mineral oil containing 5 per cent of rape oil. The figures as shown by the Redwood No. II were 25,000 sec for the mineral oil and 62,000 sec for the oil containing the rape oil. Thus, there can be very wide differences in viscosities at the pour point.

Mr G. Kinner: I well appreciate the difficulty of making accurate viscosity measurements at low temperatures, although I have only had an opportunity to carry out a limited number of tests. I feel the author is not altogether justified in saying that the A.S.T.M. chart is valueless for the presentation of the data obtained, simply because of the deviation of the plots from linearity at temperatures near the pour point. I think quite different values for viscosity could have been obtained on his oils merely by varying somewhat the experimental technique.

First, in my own laboratories, we use a series of Ubbelohde viscometers all of similar dimensions except, of course, for capillary diameter. It has been observed that whereas an oil may not flow, or at least flow only extremely slowly, in a No. 3 instrument at some given low temperature, the same oil will flow quite readily in the next size larger tube. This is due to the increased shearing stress imposed, and it is obvious that two totally different values for (apparent) viscosity will be obtained in the separate instruments. This technique of "stepping-up" to a larger instrument is admittedly in contrast to Mr Daniel's approach, but it has the additional practical advantage of eliminating excessively long flow-times.

Secondly, by using more complicated apparatus, I have found it possible —with SAE 10 and 30 oils—to obtain a linear relationship on the A.S.T.M. chart at temperatures well below the pour point. This has been done by using a capillary pressure viscometer when linearity was preserved to −40° F with shearing stresses as low as 100 p.s.i. During these experiments it was also noted that below the pour point the apparent viscosity of the oils was much less dependent upon change in rate of shear than was the case with mineral jelly tested at room temperature. This appears to be support for Mr Daniel's observations regarding the more concentrated type of dispersion of greater rigidity.

When Mr Daniel was introducing his paper, I understood him to say that his study was complementary to work done on actual engines. It would be of great interest to know how far his results were found to be significant in practice. In my own experience, the effect of moderate changes in viscosity of engine lubricating oil is entirely obscured by other factors at very low temperatures, viz., difficulties with carburation and ignition of the fuel.

The rate of cooling to which Mr Daniel has referred is also a subject of very considerable practical importance. During the first world war, a tremendous

amount of castor oil was used for aero engines. Very serious difficulties were encountered in the field with the storage of castor oil at low temperatures. The problem therefore arose how to produce castor oil which would withstand the storage conditions. The problem was solved by the introduction of castor oil, which was castor oil with an addition of a small quantity of a polymerized castor, about 5 per cent. I am not certain about the percentage exactly, but it was of that order.

With regard to the rate of cooling, Holde published some results (*Chem. Zeit.*, 1902, 176). He found that when petroleum which gave a solid deposit at −10° C but did not solidify was kept at that temperature for 1 hr and then cooled to −12° C, a large amount of solid separated but the oil remained fluid. If it were cooled to −12° C directly the whole of it became solid. Apparently in the first cooling there was opportunity for the solids to settle, with the result that on further cooling there was insufficient solid matter produced to destroy the oil's "fluidity." That indicates that with a small variation of temperature of only 2° one can obtain very different results in regard to pour point.

Reference has been made to the effect of a pour-point depressant, and some extremely interesting points of view have been advanced. I am sure that many of you will wish to pursue this subject. But first I would like to tell you of some results which I have found. The pour-point depressant with certain oils—I will not say it is universally so because I do not know—did not show its maximum efficiency for several weeks. I think the variation was as much as 10° to 15° F in the pour point. What I am suggesting is that, supposing the figure is −10° F after 24 hr of blending, it may easily drop to −25° F after a month's standing. So any figures taken on a newly blended oil will not necessarily be the correct figures when the customer receives the oil.

I would like to ask whether, in the pressure viscometer, the solubility of air has any effect on the viscosity results. It is a subject which is becoming important, particularly with the hydrogen cooling of electric generators at the present time. It is quite conceivable that under the pressures referred to—400 to 500 cm of mercury—the solubility of the air would be quite appreciable.

Also I should like to ask Mr Daniel whether in his view the adsorption of the pour-point depressant, and its effect on the size of the crystal and the amount of crystal which is formed, is a new idea, or whether it is something which has been established for some time?

We shall welcome any comments which any one present would care to offer on this very important paper.

Mr E. T. Thornton: With regard to the theory to explain why the flow is better when the pour-point depressant is present, is it possible that what comes out is not the original wax but some combination? In view of the remarks of Mr Kinner about the jellies, it seems that the factor may not be the structure alone, but also the strength of the particles making up the structure. It is quite possible that the reason why some suspensions do not offer the same resistance to the higher stress as is offered by others, is that the particles themselves are softer and can be squashed about and made to flow. Has any work been done on different

kinds of waxes? Do you know anything about the hardness of precipitated wax? What comes out? Is it the original wax, or is there first a solid which is neither the wax nor the depressant, but some combination which is itself softer?

THE PRESIDENT: In the type of oil used in aircraft engines I should imagine that there would be a difference in the hardness of the wax in different supplies.

MR THORNTON: I do not think the wax is necessarily of the same kind; it comes out at a different temperature.

MR G. H. THORNLEY: I am interested in the point raised by Mr Thornton, that something comes out from the pour-point depressant, because the use of pour-point depressants has led to some anomalies in the so-called floc test, which is becoming popular for refrigerator oils. An oil having a pour point of, say, $-20°$ and a floc test of $-10°$ without a pour point depressant will give, with a pour-point depressant, a pour point of $-30°$ ($10°$ lower) and a floc test of zero ($10°$ higher).

Reference has been made by Mr Daniel to one particular pour-point depressant; but there are other sorts. There is the pour-point depressant which naturally exists in the oil and can be removed by heavy clay treatment; and there is the acrylic polymer type of depressant, similar to some of the additives which are viscosity index improvers.

MR A. J. F. KENYON: In the Esso European Laboratories we use a low temperature apparatus which was developed by the Standard Inspection Laboratories in America. This apparatus (Fig. 1) is a little more

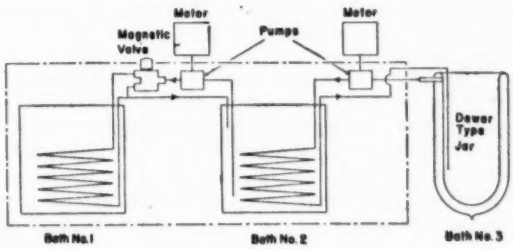

FIG. 1.

automatic in its operation than that used by Mr Daniel. Manual control is eliminated, giving a fine temperature regulation. There are three baths, the first bath containing *iso*propyl alcohol is cooled by means of solid CO_2 to a temperature considerably lower than the desired operating temperature. The second bath is cooled by circulating its contents through a cooling coil immersed in the first bath. The temperature is maintained at $5°$ to $10°$ lower than the test temperature by means of a regulator, magnetic by-pass valve, and a small immersion heater. The final bath consisting of a Dewar-type vessel is cooled by means of a coil

immersed in the second bath, the final fine control being obtained by a regulator and 100-W low-lag heater. The use of a Dewar-type jar rather than an insulated glass container gives better insulation and less trouble from condensation. With this instrument control within $\pm 0{\cdot}1°$ can be maintained merely by the periodical addition of solid CO_2 to the first bath.

DR G. B. MAXWELL: The question of the behaviour of waxy fuels is of great practical importance to people who have to pump such fuels at varying temperatures. Explanations of the behaviour of aviation lubricants at low temperatures tie up very closely with the generally accepted explanation of the anomalous behaviour of fuel oils. However, fuel oils have to be pumped in the unused state in refineries, but in the case of a lubricant, its major period of operation in the engine is in the used condition rather than the unused.

In connexion with the actual pouring of unused lubricating oils from containers in the field we can take precautions—for instance, in many cases it is arranged to store the lubricants under warm conditions. Inside the engine, after a very short period of operation, the lubricating oil has changed very considerably. I would ask Mr Daniel whether he has attempted any work on the same lubricants before and after they have been in use in the engine for a short time, because the breakdown products that are likely to be dispersed in the lubricants may have a profound effect on the low-temperature behaviour of the lubricants. Any estimates he may make on the startability of an engine from determinations of viscosity of the unused oil at various rates of shear may be misleading when the same lubricant has been used in an engine.

At the same time I would ask whether any similar work has been done on detergent oils after use, because the additives would affect the amount of breakdown products which would be dispersed through the oils after they had been in use for some time.

MR J. F. T. BLOTT: I was very interested in the effect of storage at ordinary temperatures, where the viscosity at low temperatures depended very much on the time of storing at the higher temperatures. I suppose there was no obvious separation of solids at the storage temperature, that there was no building up of solid particles. Yet the effects of storage could be eliminated by agitation. Has Mr Daniel any ideas with regard to the possible mechanism?

THE PRESIDENT: I am wondering whether Mr Kinner could help with regard to the question that has been put concerning used oils. Have you had experience of the inspection of used oils?

MR G. KINNER: I have no experience from the low temperature point of view. We inspect used oils regularly, after given mileages and so on, but do not find any significant changes in pour point even after the oil has deteriorated to a considerable extent.

THE PRESIDENT: I think Mr Maxwell's suggestion was that when the oil has been in use for a while a lot of these difficulties disappear.

DR G. B. MAXWELL: I think it may quite easily affect the wax lattice structure, just as we know that the more complete refining of lubricating oil will affect the low-temperature properties by removing particular substances. But it seems, from the practical standpoint, that we are interested in how a lubricating oil will behave in an engine, not merely when the engine is starting up with new oil but in subsequent use.

MR S. R. PETHRICK (written contribution): The bulk density of a solid in a liquid decreases as the particle size decreases if the particles are not spherical in shape, *i.e.*, for a given weight of solid the aggregate volume it occupies is greatest when the particle size is at a minimum. It follows from Einstein's law that when the material has the greatest aggregate volume it will give rise to the maximum viscosity of the suspension. When a solution of wax in oil is chilled suddenly, the particles are deposited in a state of small size and large aggregate volume. The viscosity of such systems will be higher than that of the system in which the wax particles are large as a result of slow cooling. In addition to this simple mechanism the viscosity of a suspension is increased by the solid particles carrying with them layers of liquid from the continuous phase, *i.e.*, the effective concentration of wax is increased by the removal of some of the liquid. The amount of liquid removed will be proportional to the aggregate surface of the solid, which is greatest for the smaller particles. If we assume that the layers of liquid adhere to the surface of the wax crystal it is possible to explain the action of pour-point depressants by assuming preferential adsorption of the depressant. In such a case the removal of continuous phase is minimized. If the pour-point depressant re-dissolves in the oil at a temperature higher than the melting point of the wax pour-point depressant action can be eliminated by the following cycle of operations: (*a*) cool oil below pour point; (*b*) heat to melting point of wax; and (*c*) re-cool. After such operations the depressant is out of solution, but not deposited on the wax crystal. This type of mechanism explains the thermal sensitivity of fuel oils containing asphaltic matter and wax.

THE PRESIDENT: I was hoping that someone would challenge the adsorption theory.

MR BLOTT: If I may comment on the remarks of Mr Pethrick, surely the problem is not just that of the amount of wax that comes out. I do not think this increase of viscosity can be explained by Einstein's law. It is rather a question of whether the wax crystals build up as a structure or network. Mr Daniel has shown very clearly, and, in fact, has proved, that the same amount of wax comes out, with or without the pour-point depressant, but that he does not find the same viscosity in both cases.

MR D. R. BAILEY: I would like to endorse some of the remarks of earlier speakers on the similarity in behaviour between the oils described by Mr Daniel and some oil fuels. I imagine that the wax content of the oils examined by Mr Daniel was relatively low and would suggest that by

comparison the anomalous viscosity effects with some fuel oils are greatly magnified. This raises important problems in the handling of fuel oils, particularly if one wishes to pump fuel through an under-water line a mile long.

With fuel oils showing anomalous viscosity effects, the pour point is unreliable as a criterion of pumpability, and there is some evidence, as suggested by other speakers, that the nature of the wax is a possible reason for the anomalous flow characteristics of some fuel oils. I would stress the great value to handling and marketing organizations of an extension of work such as that described by Mr Daniel to cover fuel oils.

MR R. A. FRASER: An earlier speaker has referred to the use of viscosity-index improvers. Has Mr Daniel carried out any work on the effects of these improvers? When doing some work on such improvers we found that, if we plotted the viscosity–temperature curve on an A.S.T.M. chart for an oil containing one of the polymerized improvers, the curve was not linear at the upper end. At temperatures of about 200° F there is a deviation from linearity, probably due to de-polymerization as temperature increases. Furthermore, I believe it is a fact that at high rates of shear these polymers tend to undergo depolymerization; therefore, it would be very interesting to know what sort of results Mr Daniel would get in his pressure viscometer with oils containing these additives.

MR DANIEL, replying to the discussion, said: The point has been raised by the President concerning the effect of dissolved air in the pressure viscometer. The solubility of air in these heavy lubricating oils at 20° C is of the order of 9 per cent by volume at atmospheric pressure; thus, at equilibrium, at 100 lb/sq. in. pressure one would expect an oil to contain about 60 per cent of its own volume of dissolved air. However, bearing in mind the high viscosity of the oils and the comparatively small oil–air interface, it is very unlikely that much air would pass into solution in the time during which the oil is under pressure. So I very much doubt whether this factor has had any effect on the results. Whether or not it would have any effect if it were possible for the air to pass into solution I do not know, but I feel it is unlikely.

I quite agree with Mr Kinner in that one would expect different results for different capillaries when using Ubbelohde viscometers at low temperatures. Although I did not stress the point when introducing the paper this evening, I mentioned that all the results obtained at temperatures below about 10° C were obtained in the same (actually a No. 4 Ubbelohde) viscometer in order to eliminate such differences. Although the rate of shear and shearing stress is very low in these viscometers, it is obvious from Figs. 12 and 13 that a small change would have an appreciable effect on the apparent viscosity. However, the change brought about by using a larger capillary would be relatively small compared with the large change occasioned by the use of a high shearing stress. In passing, I would point out that Ubbelohde viscometers are not entirely suitable for use at low temperatures with non-Newtonian liquids because the shearing stress, which is determined by the head of liquid, is not constant.

As regards the use of the A.S.T.M. chart, I did not mean to imply that it is completely valueless at low temperatures; but we must use it with caution and bear in mind the conditions under which we are determining the viscosity. My results would tend to suggest that at the very highest rates of shear the A.S.T.M. plots would be practically linear at the lowest temperatures, except perhaps in cases where large quantities of wax are thrown out of solution. Incidentally, if no solid matter is deposited from an oil, then, using a pressure viscometer, a linear A.S.T.M. plot is to be expected even at temperatures below the pour point.

Coming to the practical considerations from the engine point of view, owing to the pressure of other work the majority of the engine tests which it was intended to carry out, complementary to the laboratory investigations of the viscosity, have not been made, so that it is not possible for me to say very much on that aspect.

The suggestion has been made by Mr Thornton that when a pour-point depressant has been added to an oil, it is not merely wax that comes out, but a combination of wax and the depressant. I think this is a possibility, but, on the whole, the weight of experimental evidence indicates that the additive functions through adsorption on the surface of the wax. For example, it has been shown by Bondi that the depressant is relatively ineffective when an oil is chilled. Since chilling results in the formation of small crystals with a large total surface area, this indicates that the additive is associated with the surface of the crystals rather than in a homogeneous combination (or mixture) with the wax. Assuming then that surface adsorption occurs, then the additive must function either by preventing crystals sticking together themselves or by enabling the crystals to slide past each other more easily. I think it would be very difficult to differentiate between these two mechanisms practically; one would have to know considerably more about the mode of adsorption of the depressant on the crystals before one could draw any very definite conclusions.

The apparatus illustrated by Mr Kenyon represents certainly a very great improvement on the one we used. We had to make the best use of material available at the time, and our apparatus was somewhat cumbersome; the adjustment of valves, and so on, became a little tedious at times, and we had to watch the temperature continually. Had we intended to carry out further work using Ubbelohde viscometers at low temperature, we should have constructed an apparatus which would have eliminated manual temperature control.

We did not carry out tests on used engine oils; but I can quite appreciate that the combustion products, etc., which become dispersed in the oil after it has been in an engine for only a very short time would probably have an appreciable effect on the low-temperature viscosity.

With regard to the point raised by Mr Blott concerning storage, I cannot give any explanation of the results. There was no obvious separation of solids at the storage temperature, and the change in viscosity after agitation is most puzzling.

Although, as Mr Pethrick states, a suspension of small, non-spherical particles in a liquid will possess a higher viscosity than a similar suspension containing the same weight of larger particles owing to the increased

aggregate volume, I think it unlikely that the large differences between the viscosity of chilled and slowly cooled oils can be explained by Einstein's law, or some modification of it. The viscosity of a chilled oil can be more than 100 times greater than that of the cooled sample. The aggregate volume of the wax will no doubt have its influence on viscosity, but I think this effect is overwhelmed by the formation of some type of network by the wax crystals which imparts a rigidity to the oil giving rise to high viscosity at low shearing stresses.

We did not carry out any tests on oils containing viscosity index improvers. I do not think the rates of shear employed in the pressure viscometer would have been sufficiently high to disintegrate the molecules of the viscosity index improvers themselves. One would need to go to very high rates of shear, possibly of the order of 10^5 or 10^6 sec^{-1} in order to bring about disintegration of these molecules.

Vote of Thanks.

The President: It is perfectly clear that Mr Daniel has dealt with his subject very admirably; it is a subject which is of importance, particularly now that high-altitude flying is becoming much more extensive and arctic conditions are occupying the thoughts of some of us.

He has closed temporarily the problem of pour point and the effect of dilution; but certainly he has opened a very big door for investigation into the adsorption of pour-point depressants. I am sure the physical chemists will want to investigate that subject, because it is of tremendous importance in the whole field of additives.

It is my very great pleasure to offer our thanks to Mr Daniel for having given us this very interesting paper; I am sure you will all wish to associate yourselves with me in expressing our thanks.

(The vote of thanks was accorded with enthusiasm, and the meeting closed.)

OIL-SOLUBLE SODIUM NAPHTHASULPHONATES. SOME OBSERVATIONS ON THEIR CHEMICAL NATURE.

By V. W. David.*

Summary.

Medicinal oil sodium naphthasulphonates, which are useless as emulsifiers, and technical white oil sulphonates, which are good emulsifiers, consist of the same group of sulphonates according to Pilat's classification based on the solubility characteristics of their calcium derivative. The solubility characteristics of their barium, lead, aluminium, and iron derivatives are also similar. It has been found that the two grades of product can be readily differentiated by studying their behaviour on extracting an alkaline aqueous solution of their sodium salts with petroleum ether. Under these conditions both grades can be separated into two fractions which are, respectively, soluble in alkaline aqueous alcohol and soluble in petroleum ether. The former, Component I, including that derived from medicinal oil sulphonates, is a useful emulsifier, whereas the latter fraction, Component II, is always devoid of any emulsifying properties. Medicinal oil sulphonates are characterized by a high content of Component II, whereas technical white oil sulphonates are characterized by a high content of Component I. The isolation of valuable emulsifying components from unsatisfactory products is also described.

Introduction.

Oil-soluble sodium naphthasulphonates, sodium petroleum sulphonates or "mahogany soaps" are obtained as a by-product during the manufacture of technical white oil and medicinal oil. Treatment of the appropriate feedstock with oleum results in the formation of an upper oil layer containing oil-soluble naphthasulphonic acids or "mahogany acids," and a lower acid-sludge layer containing oil-insoluble naphthasulphonic acids or "green acids." The oil-soluble sulphonic acids are generally isolated from the oil layer as the crude sodium salt by treatment of the "sour" oil layer with an aqueous alcoholic solution of caustic soda followed by recovery of the solvent. The crude salt is then generally purified.

Oil-soluble sodium naphthasulphonates have found extensive use as wetting agents and as emulsifiers in soluble-oil compositions. The effectiveness of the salts as emulsifiers depends on the method of manufacture and the mean molecular weight of the feedstock. It has been found, for instance, that the oil-soluble sodium naphthasulphonates obtained during the manufacture of technical white oil are, in general, good emulsifiers, whereas those obtained during the manufacture of medicinal oil are poor emulsifiers. To assist in the disposal of the unsatisfactory emulsifiers, a clearer understanding of the chemical differences between the unsatisfactory and satisfactory types of naphthasulphonates was sought, and this communication records some new observations on the chemical nature of oil-soluble sodium naphthasulphonates.

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* "Shell" Refining and Marketing Co. Ltd.

Discussion.

Naphthasulphonic acids were originally classified by Pilat *et al* into three types : α-, β-, and γ-sulphonic acids according to the solubility of their calcium salts in ether and water.[1] The oil-soluble β-sulphonic acids, the calcium salts of which are ether-soluble but water-insoluble, were later subdivided into β- and δ-sulphonic acids according to the colour produced with ferric chloride.[2] From an aqueous solution of the sodium β-sulphonates a petroleum-ether-insoluble complex is precipitated on treatment with ferric chloride. This complex imparts an intense blue colour to diethyl ether in which it is soluble. The corresponding iron complex of δ-sulphonic acids imparts a yellow-green colour to diethyl ether. This complex is, however, soluble in petroleum ether. β-sulphonic acids have been found to consist of complex phenol sulphonic acids.[3]

More recently Sperling [4] has shown that petroleum sulphonic acids can be subdivided into oil-soluble monosulphonic acids and oil-insoluble mono- and di-sulphonic acids. The oil-insoluble acids are found in the acid sludge. On diluting the latter with water an oily upper layer is obtained containing the mono-sulphonic acids as well as some disulphonic acids. The remaining highly aromatic disulphonic acids are found in the dilute mineral acid lower layer. The latter disulphonic acids are stated to correspond to Pilat's γ-sulphonic acids.

Solubility Characteristics of Metal Salts of Oil-soluble Naphtha Sulphonic Acids.

The determination of the solubility characteristics of the oil-free calcium salts of a representative sample of (*a*) technical white oil naphthasulphonates typifying a satisfactory emulsifier, (*b*) medicinal oil naphthasulphonates typifying an unsatisfactory emulsifier, both produced at the Stanlow Refinery from naphthenic feedstocks of Venezuelan origin, showed that both grades consisted almost entirely of ether-soluble, water-insoluble sulphonates. The purified sodium salts failed to give the charac'eristic

Table I.

A.S.T.M. Analysis Data on Commercial Oil-soluble Sodium Naphthasulphonates.

Components.	Technical white oil naphthasulphonates.	Medicinal oil naphthasulphonates.
Mineral oil, per cent wt . . .	17·3	16·1
Sodium naphthasulphonates, per cent wt	68·9	66·6
Sodium carboxylates,* per cent wt .	2·8	1·6
Inorganic salts (alcohol insoluble) (as Na_2SO_4), per cent wt . . .	2·5	4·5 †
Alkali (as NaOH), per cent wt . .	0·2	0·0
Water, per cent wt	7·9	12·5
Equivalent weight of sulphonic acids .	439	478

* Sodium naphthasulphonates are always contaminated with small quantities of the sodium soaps of carboxylic acids of unknown constitution. The acids are probably produced during the sulphonation reaction. Their sodium soaps are referred to as "sodium carboxylates" and are assumed to have an equivalent weight of 334.

† This figure includes 0·7% wt iron impurities calculated as Fe_2O_3.

colour reaction of Pilat's β- and δ-sulphonic acids with ferric chloride, but since the iron complex was in both cases soluble in petroleum ether they can be said to resemble closely Pilat's δ-sulphonic acids. Similar solubility determinations were made with the barium, lead, aluminium, and iron salts of the two grades of products. A determination could not be made with the tin salts since they were colloidal. Since in all cases the two grades of product behaved alike, it was concluded that this line of approach was not likely to succeed in elucidating any chemical differences between useful and useless naphthasulphonates emulsifiers. Table I gives the analysis data obtained by the A.S.T.M. method (D855-45T) on the two grades of product. Table II summarizes the solubility data obtained.

TABLE II.

Solubility Data of Metal Salts of Oil-soluble Naphthasulphonic Acids.

	Ca.	Ba.	Pb.	Al.	Fe.
	Technical white oil naphthasulphonates.				
Ether soluble, per cent wt	92·0	93·5	96·0	>96·2	>90·0
Water and ether insoluble, per cent wt	0·0 *	1·5	1·3	0·0	0·0
	Medicinal oil naphthasulphonates.				
Ether soluble, per cent wt	91·0	93·0	94·0	>94·4	>90·0
Water and ether insoluble, per cent wt	0·0 *	5·5	6·8	0·0	0·0

* A small quantity of water-soluble calcium soaps was also found to be present.

TABLE III.

Analytical Data of Aluminium Salts of Oil-soluble Naphthasulphonic Acids.

	Technical white oil naphthasulphonates (equivalent wt of RSO_3Na = 461).	Medicinal oil naphthasulphonates (equivalent wt of RSO_3Na = 500).
Wt of RSO_3Na taken, g	(i) 0·494 (ii) 0·514	(i) 0·496 (ii) 0·519
Wt of ether-soluble Al salt isolated, g	(i) 0·514 (ii) 0·536	(i) 0·510 (ii) 0·522
Ether-soluble Al salt as $(RSO_3)_3Al$, per cent	(i) 107 (ii) 107·5	(i) 106 (ii) 103·5
Ether-soluble Al salt as $(RSO_3)_2Al(OH)$, per cent	(i) 104 (ii) 104·5	(i) 103 (ii) 101
Ether-soluble Al salt as $(RSO_3)Al(OH)_2$, per cent	(i) 96·1 (ii) 96·4	(i) 95·3 (ii) 93·5
Ash on ether soluble Al salt (as $Al_2(SO_4)_3$), per cent	21·2	17·1
Ash as $Al_2(SO_4)_3$, calculated on basis of $(RSO_3)_3Al$, per cent	12·7	11·7
Ash as $Al_2(SO_4)_3$, calculated on basis of $(RSO_3)_2Al(OH)$, per cent	18·5	17·1
Ash as $Al_2(SO_4)_3$, calculated on basis of $(RSO_3)Al(OH)_2$, per cent	34·2	31·8

The observations made with aluminium and iron salts deserve comment. On the basis of the equation

$$3RSO_3Na + AlCl_3 \longrightarrow (RSO_3)_3Al + 3NaCl$$

there should be a loss of 42 g per gram molecule on converting the sodium naphthasulphonates into the aluminium salts. In actual fact an increase in the weights of the isolated ether-soluble aluminium salts was obtained. The analytical data (see Table III) suggest that basic aluminium salts were obtained, the average composition of which corresponds approximately to that of a monobasic salt, $(RSO_3)_2Al(OH)$.

The average composition of the iron naphthasulphonates was also found to correspond approximately to a monobasic salt (see Table IV).

TABLE IV.

Analytical Data of Iron Salt of Oil-soluble Naphthasulphonic Acids.

	Technical white oil naphthasulphonates.	Medicinal oil naphthasulphonates.
Ash on ether-soluble Fe salt (as Fe_2O_3), per cent	9·4	8·9
Ash, as Fe_2O_3, calculated on basis of $(RSO_3)_3Fe$, per cent	5·8	5·4
Ash, as Fe_2O_3, calculated on basis of $(RSO_3)_2Fe(OH)$, per cent	8·4	7·8
Ash, as Fe_2O_3, calculated on basis of $(RSO_3)Fe(OH)_2$, per cent	15·1	14·1

Solubility Characteristics of Sodium and Potassium Salts of Oil-soluble Naphthasulphonic Acids in Alkaline Aqueous Alcoholic Solutions.

During the course of some other experiments it was observed that, whereas no sulphonates can be extracted with petroleum ether from a neutral aqueous alcoholic solution of "pure" (*i.e.*, oil free) medicinal oil and technical white oil sodium or potassium naphthasulphonates, the two grades of product showed considerable difference in solubility on extraction of alkaline aqueous alcoholic solutions of the salts with petroleum ether. In this manner the sodium naphthasulphonates were separated into two components. The fraction which cannot be extracted with petroleum ether from the aqueous alcoholic alkaline solution of the oil-free sodium naphthasulphonates is termed Component I; the fraction which can be extracted with petroleum ether is termed Component II.* The presence of Component II in the aqueous alcoholic caustic-soda (or potash) solution makes the latter turbid at high concentrations of alkali (greater than 1 to 2 per cent w/v caustic soda in 50 per cent aqueous alcohol depending on grade of sulphonates used), though the solution remains clear at lower concentrations of alkali. The various fractions of Component I and Component II isolated were examined for their suitability as emulsifiers in a standard soluble-oil composition. The results of the separation experiments, using

* In British Patent Application No. 9764/47 these fractions have been referred to as "petroleum-ether-insoluble constituents" and "petroleum-ether-soluble constituents" respectively.

an arbitrarily fixed concentration of both caustic potash and alcohol (industrial methylated spirit), viz., 0·6 g potash per 100 ml 50 per cent aqueous alcoholic solution containing 5 g oil-free sodium naphthasulphonates, are given in Tables V and VI. Experimental details are similar to those described in the next section.

TABLE V.

Components I and II from Technical White oil Sodium Naphthasulphonates.

No.	Sulphonates content—A.S.T.M.,* % wt.	Performance of soluble oil prepared from commercial product.	Component II, % wt.		Performance of soluble oil prepared from	
			On total sulphonates.	On sample.	Component I.	Component II.
1	74·5	Highly dispersed	16·7	12·4	Highly dispersed	Complete failure
2†	71·7	Milky; satisfactory	34·0	24·4	Superior to original; highly dispersed	Complete failure
3	76·0	Complete failure	53·6	40·7	Highly dispersed	Complete failure

* Values include small carboxylate content. No carboxylic acids were added during the manufacture of the products.

† For complete analysis of this sample see Table I.

TABLE VI.

Components I and II from Medicinal oil Sodium Naphthasulphonates.

No.	Sulphonates content—A.S.T.M.,* % wt.	Performance of soluble oil prepared from commercial product.	Component II, % wt.		Performance of soluble oil prepared from	
			On total sulphonates.	On sample.	Component I.	Component II.
4†	68·2	Complete failure	71·0 71·4	48·3 48·7	Highly dispersed	Complete failure
5	53 (approx)	Complete failure	82·0 (approx)	43·5	Good dispersion; tendency to cream on standing	Complete failure
6	53	Unsatisfactory; gels	71·0	37·6	Highly dispersed	Complete failure

* Values include small carboxylate content. No carboxylic acids were added during the manufacture of the products.

† For complete analysis of this sample see Table I.

The results given by both grades of product show that Component I has good emulsifying properties, whereas Component II is useless as an emulsifier.

The two components are present in different proportions in the two grades of sodium naphthasulphonates. Medicinal oil sodium naphthasulphonates are characterized by a high Component II content (>70 per cent wt of total sulphonates) whereas technical white oil sodium naphthasulphonates are characterized by a high Component I content (>65 per cent wt of total sulphonates). A batch of inferior technical white oil sodium naphthasulphonates gave an intermediate value for the content of Component II.

The Effect of Alkali Concentration on the Solubility Characteristics of Sodium Salts of Oil-soluble Naphthasulphonic Acids in Alkaline Aqueous Alcoholic Solutions.

The effect of alkali concentration on the relative proportion of Component I and Component II in technical white oil and medicinal oil sodium naphthasulphonates has been studied in detail. Equivalent weight determinations and emulsifying tests were carried out on the many fractions isolated in the course of this study. Experimental details are as follows:

Isolation of Components I and II.

(a) *Removal of Mineral Oil.* This was carried out on lines similar to those used in the A.S.T.M. method. $10 \pm 0{\cdot}1$ g of sodium naphthasulphonates were dissolved in 50 ml hot 50 per cent aqueous alcohol in a small beaker. The aqueous alcohol contained sufficient hydrochloric acid to neutralize the small alkalinity of the sample, if any. The alcohol solution was transferred quantitatively into a separating funnel, the beaker being rinsed with a further 50 ml of 50 per cent aqueous alcohol. The combined aqueous alcoholic solution was then extracted with several (usually 6 to 8) portions of 50 ml petroleum ether (40 to 60° C) until the ether layer was quite colourless. The combined ether extracts were then washed with 2 to 4 25-ml portions 50 per cent aqueous alcohol. All alcohol layers were then combined giving a total volume 150 to 200 ml.

(b) *Isolation of Component II.* The alcoholic solution was diluted in such a way that a total volume of 300 ml 50 per cent aqueous alcohol was obtained, containing varying amounts of alkali ranging from 0·1 to 1·5 g caustic soda per 100 ml 50 per cent aqueous alcohol, a normal solution of caustic soda being employed. For the higher concentrations of alkali, however, 2*N*-caustic soda had to be used in order that the total volume of the solution should not exceed the arbitrarily fixed volume of 300 ml. The aqueous alcoholic alkali layer was then extracted with several (usually 3 to 6) portions of 50 ml petroleum ether (40 to 60° C) until the ether layer was quite colourless. The ethereal solution was then filtered, and the solvent evaporated in a large hemispherical gum dish on a steam-bath. The residue was repeatedly washed with acetone to remove water and then dried in an oven at 105° C to constant weight.

(c) *Isolation of Component I.* The combined aqueous alcoholic soda layer was evaporated to small bulk; this removed all the alcohol present. The aqueous layer was then strongly acidified and extracted with ethyl ether. The ethyl ether extract was washed repeatedly with 25 per cent sodium chloride solution to remove mineral acids and to convert the sulphonic acids into their sodium salts. The ethyl ether layer was then dehydrated

with excess anhydrous sodium sulphate, filtered, the solvent removed, and the residue dried as in (*b*) above.

Equivalent Weight Determinations.

The mean equivalent weights of the various fractions of Components I and II were obtained by determining the sulphated ash content of these fractions. Since, from the mode of preparation, it was expected that Component II would be practically free from sodium sulphate and alkali no corrections were applied. The fractions of Component I, on the other hand, were all subjected to a desalting process according to a modified form of the A.S.T.M. procedure as follows :—

The sulphonate fraction was dissolved in 50 per cent aqueous *iso*propyl alcohol and heated to approximately 50° C in a small separating funnel. 18 g anhydrous sodium carbonate (A.R.) per 100 ml alcoholic solution was then carefully admitted to the solution. The funnel was shaken vigorously for 5 min, venting frequently. The phases were then allowed to separate at approx 50° C for 1 to 2 hr. The salt layer was withdrawn, and the alcohol layer allowed to cool overnight. It was then filtered, and aliquot portions of the filtrate were evaporated to dryness in tared ash dishes.

In addition, a carboxylate correction was applied to fractions of Component I, it being assumed that the carboxylate soaps in the original products would remain soluble in the aqueous alcoholic phase. As in the A.S.T.M. method the equivalent weight of the sodium carboxylates was assumed to be 334.

The results are given in Table VII and Figs. 1 and 2.

TABLE VII.

Effect of Caustic Soda Concentration on the Relative Proportion of Components I and II, their Emulsifying Power and Equivalent Weights in Two Grades of Sodium Naphthasulphonates.

NaOH/ 100 ml 50% aq. alcohol.	Component II, % wt on total sulphonates.		Equivalent weight.				Performance of soluble oil prepared from	
			Component I.		Component II.			
g.	M.O.*	T.W.O.*	M.O.	T.W.O.	M.O.	T.W.O.	Component I ex M.O.†	Component II ex T.W.O. ‡
0·1	7·6	0·85	—	—	—	—	Complete failure	Complete failure
0·2	18·1	1·55	—	—	557	—	,, ,,	,, ,,
0·3	24·4	6·7	470	440	—	558	,, ,,	,, ,,
0·4	33·1	14·1	472	—	543	526	Readily emulsifies	,, ,,
0·5	40·9	16·0	—	—	—	—	,, ,,	,, ,,
0·6	56·8	23·5	454	—	520	495	Highly dispersed	,, ,,
0·7	57·6	26·1	—	—	510	—	,, ,,	,, ,,
0·8	62·4	35·7	—	—	499	—	,, ,,	,, ,,
0·9	66·1	37·2	—	—	498	483	,, ,,	,, ,,
1·0	62·3	34·3	—	—	—	—	,, ,,	,, ,,
1·1	68·7	43·5	—	—	486	469	,, ,,	,, ,,
1·2	67·6	43·1	—	—	—	—	,, ,,	,, ,,
1·3	68·9	50·2	454	439	484	463	,, ,,	,, ,,
1·5	—	50·3	—	—	—	451	,, ,,	,, ,,

* M.O. = Medicinal oil sodium naphthasulphonates : T.W.O. = Technical white oil sodium naphthasulphonates.
For full analysis of the two grades of product see Table I.
† Soluble oils prepared from the corresponding Component II were useless as emulsifiers.
‡ Soluble oils prepared from the corresponding Component I were excellent emulsifiers.

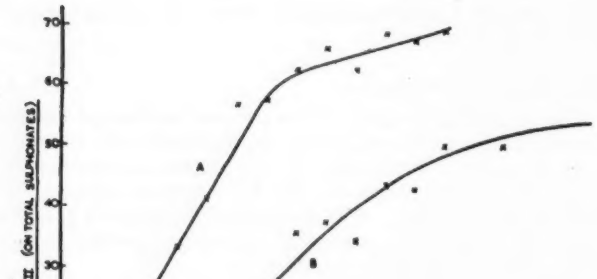
% WT. COMPONENT II (ON TOTAL SULPHONATES)
A: MEDICINAL OIL NAPHTHASULPHONATES.
B: TECHNICAL WHITE OIL NAPHTHASULPHONATES.
GRAMS NaOH/100 ml 50% AQUEOUS ALCOHOL.

FIG. 1.

EFFECT OF ALKALI CONCENTRATION ON PERCENTAGE COMPONENT II OF TWO GRADES OF OIL-SOLUBLE SODIUM NAPHTHASULPHONATES.

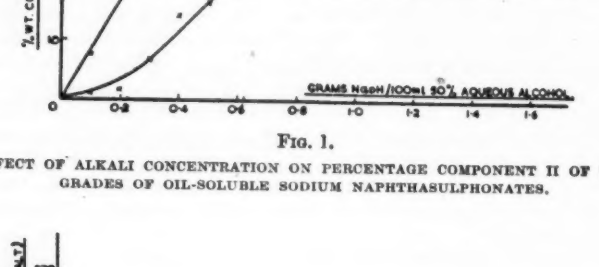
EQUIVALENT WEIGHT OF COMPONENT II (SODIUM SALT)
A: MEDICINAL OIL NAPHTHASULPHONATES.
B: TECHNICAL WHITE OIL NAPHTHASULPHONATES.
MEAN EQUIV. WT. OF ORIGINAL SAMPLE OF A.
MEAN EQUIV. WT. OF ORIGINAL SAMPLE OF B.
GRAMS NaOH/100 ml 50% AQUEOUS ALCOHOL.

FIG. 2.

EFFECT OF ALKALI CONCENTRATION ON EQUIVALENT WEIGHT OF COMPONENT II OF TWO GRADES OF OIL-SOLUBLE SODIUM NAPHTHASULPHONATES.

It is evident from these results that in an aqueous alcoholic alkaline solution of oil-free sodium naphthasulphonates the concentration of alkali influences the relative proportion of Component I and Component II which is isolated from the two phases on subsequent extraction with petroleum ether. The response to a gradual increase in the alkali concentration of

the aqueous alcoholic solutions differs considerably for the two grades of sodium naphthasulphonates.

In the case of those derived from medicinal oil production there is at first a rapid increase in the proportion of Component II with increase in alkali concentration; this is followed by a region of increasing alkali concentration in which only relatively small changes in the proportion of Component II take place. Component II, which exhibits no emulsifying properties, forms the major component over most of the range of alkali concentrations examined. The mean equivalent weight of Component II ranges from approximately 560 for that isolated at the lowest alkali concentration to 485 for that isolated at the highest concentration examined (the latter value is slightly lower than the mean molecular weight of the combined sulphonates. Lack of homogenity of the sample is probably responsible for this small discrepancy). A correspondence of the solubility data and the equivalent weights of the fractions of Component II is to be observed. The corresponding values for the equivalent weight of Component I, the emulsifying properties of which progressively improve with increase in alkali concentration range from approximately 470 to 450.

On the other hand, technical white oil sodium naphthasulphonates respond much less to changes of alkalinity, and the fractions of Component I which are excellent emulsifiers form the major component over the whole range of alkali concentrations examined. Their equivalent weight remains constant at approximately 440 over this range of alkali concentration. The equivalent weight of the various fractions of Component II which are useless as emulsifiers ranges from approximately 560 for those isolated at the lowest alkali concentration to 450 for those isolated at the highest concentration examined.

It is thus evident that the equivalent weight of the sulphonates present in both grades of sodium naphthasulphonates range from approximately 440 to 560. However, only a small fraction of the technical white oil sulphonates has an equivalent weight greater than 500, while a large fraction of the medicinal oil sulphonates is in that category.

The general trend of the solubility curve of both grades of naphthasulphonates indicates that the separation process is, in fact, a "salting out" process in which progressively more and more lower molecular weight material is forced into the petroleum ether phase with increasing alkali concentration. However, the presence of two regions of response to increasing alkali concentration in the case of medicinal oil naphthasulphonates suggests that Components I and II differ, not only in their molecular weights, but also chemically—though they appear to fall within the same class of sulphonates as defined by Pilat.[1]

Different types of oil-soluble sodium salts in medicinal oil naphthasulphonates can be expected, in view of the more drastic sulphonation treatment received as compared with that customarily used with a technical white oil feedstock. Sperling [4] has recognized the presence of oxidized oil-soluble sulphonates formed by simultaneous dehydrogenation of the hydrocarbon molecule during sulphonation. Investigations are continuing to study the nature of the hydrocarbon moiety of the various components isolated in the course of this work.

The separation process for and the use of Components I and II in emulsi-

fying compositions form part of the British Patent Application No. 9764/47 and other foreign patent applications.

Acknowledgment.

The author's thanks are due to the directors of the "Shell" Refining and Marketing Co. Ltd. for permission to publish the results.

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[2] Sereda. *Petr. Z.*, 1934, **30** (19), 1.
[3] Pilat and Sereda. *Przemysl Chemiczny*, 1938, **22**, 459; *Refiner*, 1940, **19**, 50.
[4] Sperling. *Industr. Engng Chem.*, 1948, **40**, 890.

Appendix.

To enable the properties of the two grades of sodium naphthasulphonates employed in the present investigation to be related to the raw materials whence they are derived a brief outline of the manufacture of medicinal oil and technical white oil together with the more important physical properties of the distillates and raffinates and typical analyses of the finished products is given below.

Medicinal Oil.

The distillate is prepared from a wide lubricating oil cut of naphthenic origin by redistillation under vacuum. This distillate is Edeleanized and treated with large quantities of oleum, the sludge removed, and the oil neutralized with aqueous alcoholic caustic soda. After separating the spent lye, the oil is washed with aqueous alcohol to remove the remaining sodium naphthasulphonates, dried, and acid treated with sulphuric acid of 98 per cent strength. It then receives a final neutralization and after drying is earth treated. The spent lye from both neutralization stages and from the alcohol wash is used as the starting point for the preparation of the medicinal oil sodium naphthasulphonates.

Table VIII.

Medicinal White Oil—Properties of Distillate, Raffinate, and Finished Oil.

	Distillate.	Raffinate.	Finished oil.
Sp. gr. at 60/60° F	0·947	0·892	0·884
Flash point :			
P.M. closed, ° F	430	430	430
P.M. open, ° F	450	450	450
Viscosity : Red. I at 140° F, sec	240	155	—
Kin. visc. at 100° F, cs	242	120	93
Colour, Saybolt	—	—	+ 30
Pour point, ° F	—	—	− 15
Retractive index at 50° C	—	—	1·4716
Neutralization value, mg KOH/g	—	—	<0·05
Cold test	—	—	Pass
H_2SO_4 test	—	—	Pass
Sulphur test	—	—	Pass
Taste and odour	—	—	Pass

Technical White Oil.

The distillate used for the production of technical white oil is made from the same wide lubricating oil cut as is used for the production of medicinal oil distillate. This distillate is Edeleanized and the raffinate is treated with oleum, the sludge removed, and the acid oil neutralized with aqueous alcoholic caustic soda. After drying, the oil is acid treated with sulphuric acid of 98 per cent strength, and subsequently treated with earth. The spent lye from the neutralization step is the feedstock for sodium naphthasulphonate production.

TABLE IX.

Technical White Oil—Properties of Distillate, Raffinate, and Finished Oil.

	Distillate.	Raffinate.	Finished oil.
Sp. gr. at 60/60° F	0·919	0·873	0·866
Flash point :			
P.M. closed, ° F	300	300	300
P.M. open, ° F	315	315	315
Viscosity : Red. I at 70° F, sec .	150	134	118
Colour, Saybolt	—	—	+ 30
Pour point, ° F	—	—	− 50
Retractive index at 50° C . .	—	—	1·4624
Copper strip test	—	—	Pass
Odour	—	—	Pass

ESTIMATION OF GAS/OIL RATIOS FOR OIL WELLS FLOWING THROUGH SURFACE CHOKES, OR BEANS.*

By H. Gilmour (Member).

In oilfield practice adjustment of bottom-hole flowing pressure—and, consequently, of flowing differential—is often effected at wells by the introduction, or alteration, of chokes in the surface flow pipe. Where primary control is effected by means of bottom-hole chokes, adjustment is generally so obtained.

Investigations, carried out in the fields of Apex (Trinidad) Oilfields Ltd., from records and data secured at flowing wells have indicated that a relationship exists between the actual gas-flow rate in the mixture and the rate of liquid-free gas for the same pressure conditions, depending upon the value of the actual gas–oil ratio.

That is : $$\frac{\text{Actual gas rate}}{\text{Actual liquid rate}} \propto \frac{\text{Liquid-free gas rate}}{\text{Actual liquid rate}}.$$

It was also noted that deviations, obtained by graphing one against the other were attributable, in general, to wide differences in the dissolved gas–oil ratio from that normally obtaining locally. The relationship appeared to be sufficiently well-defined to warrant an attempt to express it mathematically.

The purpose of this paper is to present a relationship between the actual and the liquid-free gas rates and the gas–oil ratio and to show the degree of accuracy attained by its use in actual practice. The liquid-free gas-flow rate can be readily calculated by means of formulæ, which are developed for this purpose from tables given in " Natural Gas Handbook." [1]

Procedure.

The Newtonian formula, as modified by Laplace, for the speed of sound in a gas is assumed to be applicable to gas-and-liquid mixtures, such as are met with in oilfield practice, passing through chokes.

The formula may be expressed thus :—

$$W = \sqrt{\frac{pK}{l}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where W = velocity of sound in the medium, ft/sec,
" p = pressure, poundals/sq. ft. absolute,
" l = density, lb/cu. ft.,
" $K = \dfrac{\text{Specific heat at constant pressure}}{\text{Specific heat at constant volume}}$.

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* Paper read before Trinidad Branch, Institute of Petroleum, on September 24, 1948.

We may, then, assuming K to be a constant, applicable to both gas and mixture, equate :—

$$\text{Ratio, } \frac{\text{Velocity of mixture}}{\text{Velocity of liquid-free gas}} = \sqrt{\frac{l_g}{l_m}} \quad . \quad . \quad . \quad (2)$$

where l_g and l_m are densities of gas and mixture, respectively, at conditions in the *vena contracta* for the same pressure conditions.

The other symbols used hereafter are :—

N = No. of choke, where $N/32$ = dia of choke in inches.
S = Sp. gr. of liquid in tanks at 60° F.
G = Sp. gr. of gas at 60° F in tanks.
R = Gas/liquid ratio in cu. ft/brl at N.T.P., determined for stock tank conditions, at 60 °F and 14·7 p.s.i.a.
D = Dissolved gas–liquid ratio, cu. ft/brl at the temperature and upstream pressure, referred to N.T.P.
V = The liquid-free gas rate for gas of sp. gr. = G, through the choke for the pressure conditions and upstream temperature as pertains for the mixture, in cu. ft/day.
B = The liquid production rate, measured in tanks, in barrels/day.
Z_c = Supercompressibility of liquid-free gas of sp. gr. = G, for pressure and temperature, T_c, in *vena contracta*.
Z_1 = Supercompressibility of undissolved gas in the mixture for conditions in actual *vena contracta*.
T = Temperature at inlet, ° F absolute.
T_1 = Temperature of mixture in *vena contracta*, ° F absolute.
T_c = Temperature of liquid-free gas in *vena contracta*, ° F abs.
P = Tubing-head pressure at inlet, p.s.i.a.
T_s = Standard base temperature, 60° F, 520° R.
p = Pressure within the *vena contracta*, p.s.i.a.

The density, l_g, of the liquid-free gas, of sp. gr. = G, at conditions in the *vena contracta*, is :—

$$l_g = \frac{0{\cdot}0763\ GpT_s}{15\ Z_cT_c} \text{ lb/cu. ft.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The density, l_m, of the gas–liquid mixture passing through the choke at the same pressure conditions is :—

$$l_m = \frac{0{\cdot}0763\ RG + 350\ S}{(R - D)\dfrac{15\ Z_1T_1}{pT_s} + 5{\cdot}61} \text{ lb/cu. ft.} \quad . \quad . \quad . \quad (4)$$

$$\therefore \text{ Ratio, } \frac{l_g}{l_m} = \frac{Z_1T_1}{Z_cT_c} \frac{\left(R + D - \dfrac{5{\cdot}61\ pT_s}{15\ Z_1T_1}\right)}{\left(R + 4580\ \dfrac{S}{G}\right)} \quad . \quad . \quad . \quad (5)$$

$$\text{The ratio, } \frac{\text{Velocity of mixture}}{\text{Velocity of liquid-free gas}} = \frac{Z_1T_1B}{Z_cT_cV}\left(R - D + \frac{5{\cdot}61pT_s}{15Z_1T_1}\right) \quad (6)$$

Evaluating 5 and 6 in Equation (2), we get :—

$$\left(\frac{V}{B}\right)^2 = \frac{Z_1T_1}{Z_cT_c}\left(R + 4580\ \frac{S}{G}\right)\left(R - D + \frac{5{\cdot}61pT_s}{15Z_1T_1}\right) \quad . \quad . \quad (7)$$

If we assume that Z_1T_1 is approximately equal to Z_cT_c, then Equation (7) simplifies to :—

$$\left(\frac{V}{B}\right)^2 = \left(R + 4580\,\frac{S}{G}\right)\left(R - D + 0{\cdot}37\,\frac{pT_s}{Z_1T_1}\right) \quad . \quad . \quad (8)$$

For critical flow, when $p_1 < 0{\cdot}55P$,

$$\left(\frac{V}{B}\right)^2 = \left(R + 4580\,\frac{S}{G}\right)\left(R - D + 0{\cdot}2\,\frac{PT_s}{Z_1T_1}\right) \quad . \quad . \quad (9)$$

An approximate equation, based on heat-exchange, for T_1, is given by

$$T_1 = 0{\cdot}89T\,\frac{(R + 4580\sqrt{S/G} \times (P/p)^{0{\cdot}213})}{(R + 4580\sqrt{S/G})} \quad . \quad . \quad . \quad (10)$$

When R is small, T_1 approximates to T and when R is large, T_1 approximates to $0{\cdot}89T$, but the term $0{\cdot}37\,\frac{pT_s}{Z_1T_1}$ is numerically small, compared with R in this case and relatively unimportant, unless the pressure p is high. It is believed, therefore, that no great error arises by substituting T for T_1. By assuming an average value of 0·9 for Z_1, the term $0{\cdot}37\,\frac{pT_s}{Z_1T_1}$ resolves to $0{\cdot}415\,\frac{pT_s}{T}$. (For critical flow, it resolves to $0{\cdot}415 \times 0{\cdot}55\,\frac{PT_s}{T}$, or $0{\cdot}228\,\frac{PT_s}{T}$).

For local conditions with tubing-head temperatures of about 100° F, Equation (8) is simplified for non-critical flow to :—

$$\left(\frac{V}{B}\right)^2 = (R + 4580\ S/G)(R - D + 0{\cdot}4p) \quad . \quad . \quad . \quad (11)$$

and for critical flow to :—

$$\left(\frac{V}{B}\right)^2 = (R + 4580\ S/G)\ (R - D + 0{\cdot}21P) \quad . \quad . \quad (12)$$

If we equate $A = 4580\ S/G$ and $(D - 0{\cdot}4p) = C$, Equation (12) becomes :—

$$\left(\frac{V}{B}\right)^2 = (R + A)\ (R - C),$$

the solution of which is :—

$$R = \frac{-(A - C) + \sqrt{(A + C)^2 + \left(\frac{2V}{B}\right)^2}}{2} \quad . \quad . \quad . \quad (13)$$

The following empirical formulæ, which are derived from the graphs,[2] for solubility of natural gases in crude oil, give approximate values of D.

TABLE I.

Comparison of Measured and Calculated Gas–Liquid Ratios.

Well.	Sp. gr.		S/G.	Pressures.		Orifice-type choke, dia N in $\frac{1}{64}$ in.	Rate of production.			$A = 4580, S/G$.	$D = 1{\cdot}1D_1$.	$0{\cdot}4p$.§	$C = D - 0{\cdot}4p$.	$A + C$.	$A - C$.	$\frac{V}{10^3}$ cu. ft/day.	$\frac{2V}{B}$.	Gas–liquid ratio, R.	
	Oil (Water = 1), S_o.	Gas (Air = 1), G.*		Tubing head, P, p.s.i.a. (aver).	Down stream, P_1, p.s.i.a.		Oil, b.d.	Water, b.d.	Gas, cu. ft/day at N.T.P.									Calculated, cu. ft/brl.	Measured, cu. ft/brl.
A	0·88	0·73	1·21	390	25	6	100	—	134,000	5,530	130	85	48	5,578	5,482	299	5,980	1,350	1,340
B	0·89	0·70	1·27	235	27	11	112	—	358,000	5,810	82	52	30	5,840	5,780	610	10,890	3,290	3,200
C	0·90	0·74	1·22	1,075	35	7	520	—	410,000	5,580	258	237	21	5,600	5,560	1,125	4,320	760	790
D	0·90	0·66	1·37	390	250	8	11	—	438,000	6,250	114	100	14	6,264	6,236	448	81,460	37,700	39,800
E	0·90	0·73	1·23	925	230	2‡	40	—	27,200	5,650	230	204	26	5,676	5,624	78‡	3,900	630	680
F	0·90	0·82	1·11	307	25	8·16	307	—	127,000	5,024	96	68	28	5,052	4,996	423	2,750	380	410
G	0·92	0·72	1·28	540	230	6	197	—	130,000	5,850	122	119	—	5,850	5,850	414	4,200	680	660
H	0·90	0·68	1·32	365	275	10	53	—	410,000	6,060	108	110	—	6,060	6,060	553	20,860	7,850	7,750
K	0·90	0·70	1·29	2,215	65	8	734	—	1,590,000	5,910	458	487	−27	5,883	5,937	3,080	8,400	2,160	2,170
L	0·925	0·74	1·25	375	235	3‡	54	—	12,000	5,710	98	92	6	5,716	5,704	578‡	2,140	200	230
M †	0·90	0·68	1·40	435	70	6	40	39	172,000	6,400	63	97	−24	6,376	6,424	344	8,700	2,170	2,170

* The sp. gr. of the gas, used in the calculation, is that sp. gr. which the gas would possess, when *all* gas is passed, together with the associated liquid, to the well tanks at atmospheric pressure.

† Well M produced 50 per cent salt water. (Total liquid 79 b.d.)

‡ Should be bigger than these evaluations.

§ Evaluations of $0{\cdot}415\,\frac{PT_s}{T}$ as mentioned in text, for critical flow only it is necessary to evaluate as $0{\cdot}228\,\frac{PT_s}{T}$, while for non-critical it is $0{\cdot}4p_1$.

Due to inflexion of the curves at about 900 p.s.i., two equations are developed, as approximations for reservoir temperatures :—

$$\text{Below 1000 p.s.i. } D_1 = \frac{p^{0.8}}{25}\left(\frac{141{\cdot}5}{S} - 135{\cdot}8\right) \text{ cu. ft/brl.} \quad . \quad . \quad (14)$$

$$\text{Above 1000 p.s.i. } D_1 = \frac{p^{1.003}}{100}\left(\frac{141{\cdot}5}{S} - 135{\cdot}8\right) \text{ cu. ft/brl.} \quad . \quad . \quad (15)$$

In local comparative tests on the determination of R, any errors in the evaluation of D would normally have only a minor effect on the resultant value of R. For very low values of R and relatively high tubing-head pressures, appreciable error might be expected, if the actual value of D should deviate seriously from the calculated value. It has only been possible to test in a limited number of such cases, from which it would appear that any serious deviation of D can probably be anticipated by an abnormal value of the specific gravity of the associated gases. In Table I, well *F* represents one of the extremely few cases, where a marked deviation was observable.

For tubing-head temperatures, it has been assumed that $D = 1{\cdot}1D_1$.

Calculation of V, Liquid-free Gas-flow Rate through a Choke.

Formulæ (16), (17), and (18) are developed from tables of choke capacities, given on pp. 302–3 of Diehl's handbook.[1]

1. *For Chokes, about* 6 *in long* :

(a) *Critical flow*, $p_1 < 0{\cdot}55P$.

$$V = \frac{P}{\sqrt{GT}} \times 357\ N^2\left(1 + \sqrt{\frac{N-1}{19}}\right) \text{ cu. ft/day at } 60^\circ \text{ F}$$

and 14·7 p.s.i. where $\frac{N}{32} = \text{dia of choke in inches.} \quad . \quad (16)$

(b) *Non-Critical flow*, $p_1 > 0{\cdot}55P$.

$$V = \frac{P}{\sqrt{GT}} \times 2 \times 357 \times N^2\left(1 + \sqrt{\frac{N-1}{19}}\right) \times \sqrt{\frac{p_1}{P} - \left(\frac{p_1}{P}\right)^2} \text{ cu. ft/day} \quad . \quad . \quad . \quad (17)$$

The value of function, $N^2\left(1 + \sqrt{\frac{N-1}{19}}\right)$ can be ascertained on a base of N from Table II. The value of function, $\sqrt{\frac{p_1}{P} - \left(\frac{p_1}{P}\right)^2}$, is given for the range for which it applies in Table III.

TABLE II.
For Chokes.

Choke size, N ($N/32'' = $ Dia).	N^2.	$N^2\left(1+\sqrt{\frac{N-1}{19}}\right)$.	Daily coefficient $357\,N^2\left(1+\sqrt{\frac{N-1}{19}}\right)$.
1	1	1	357
2	4	4·211	1,503
3	9	9·671	3,453
4	16	17·46	6,233
5	25	27·63	9,864
6	36	40·23	14,362
7	49	55·31	19,746
8	64	72·91	26,029
9	81	93·04	33,430
10	100	115·8	41,341
11	121	141·2	50,408
12	144	169·1	60,369
13	169	199·7	71,293
14	196	233·1	83,217
15	225	269·2	96,104
16	256	308·1	109,991
18	324	393·5	140,480
20	400	492	175,644

TABLE III.

Values of $\sqrt{\frac{p_1}{P}-\left(\frac{p_1}{P}\right)^2}$ *and of* $\sqrt{\left(1-\frac{p_1}{P}\right)\left(0{\cdot}45+0{\cdot}55\frac{p_1}{P}\right)}$.

$\frac{p_1}{P}$.	Choke factor, $\sqrt{\frac{p_1}{P}-\left(\frac{p_1}{P}\right)^2}$.	Orifice factor, $\sqrt{\left(1-\frac{p_1}{P}\right)\left(0{\cdot}45+0{\cdot}55\frac{p_1}{P}\right)}$.
0·15	See Eq. (17)	0·6727
0·20	—	0·6693
0·25	—	0·6637
0·30	—	0·6561
0·35	—	0·6463
0·40	—	0·6340
0·45	—	0·6194
0·50	—	0·6021
0·55	0·4980	0·5819
0·60	0·490	0·5586
0·65	0·4769	0·5316
0·70	0·4583	0·5005
0·75	0·4330	0·4643
0·80	0·4000	0·4219
Not reliable $p_1/P = >0{\cdot}8$		

2. *For Orifices* $\left(\textit{thickness}, \frac{N \text{ in}}{4\times 32}\right)$:

For critical *and* non-critical flow $\left(\frac{p_1}{P} < 0{\cdot}8\right)$.

$$V = \frac{P}{\sqrt{GT}} \times 635\,N^2 \times \sqrt{\left(1-\frac{p_1}{P}\right)\left(0{\cdot}45+0{\cdot}55\frac{p_1}{P}\right)} \text{ cu. ft/day at } 60^\circ \text{ F}$$

and 14·7 p.s.i. where $\frac{N}{32}$ = dia of orifice in inches . . (18)

The value of the function $\sqrt{\left(1-\frac{p_1}{P}\right)\left(0{\cdot}45+0{\cdot}55\frac{p_1}{P}\right)}$ on a base of $\frac{p_1}{P}$ is given in Table III. The value of 635 N^2 is given in Table IV.

TABLE IV.

N.	N^2.	635 N^2.	N.	N^2.	635 N^2.
1	1	635	11	121	76,835
2	4	2,540	12	144	91,440
3	9	5,715	13	169	107,315
4	16	10,160	14	196	124,460
5	25	15,875	15	225	142,875
6	36	22,860	16	256	162,560
7	49	31,115	18	324	205,740
8	64	40,640	20	400	254,000
9	81	51,435	24	576	365,760
10	100	63,500			

Formula (13) for the estimation of the gas–liquid ratio of a mixture of gas and liquid passing through a choke applies only to a mixture of uniform density and cannot be applied directly for wells flowing by heads. Flow by heads is characterized by the delivery of alternate "slugs" of liquid

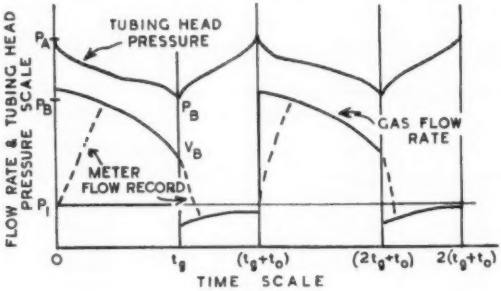

FIG. 1.

and gas. The cycle is indicated diagrammatically for critical conditions in Fig. 1.

If V_m = mean liquid-free gas-flow rate, during period, t_g, in cu. ft. at N.T.P/day,

P_A and P_B = Tubing-head pressures at beginning and end of period, t_g,

t_g = period of gas-head flow,

t_0 = period of oil-head flow,

t_c = period of cycle,

B = average rate of liquid production, b.d.

Then

$$R=\frac{V_m\times t_g}{B\times t_c}+\left[\frac{\sqrt{(A+C)^2+\left(\frac{2V_m t_0}{B\times t_c}\right)^2}-(A-C)}{2}\right]. \quad (19)$$

If there be a non-flow period during each cycle, it must be included in the evaluation of t_c.

The Value of V_m, Mean Liquid-free Gas-flow Rate.

Orifice Type Chokes.

The orifice-type choke requires only one general equation for the evaluation of V_m, whether the flow be critical, non-critical, or a combination of the two.

As given by Equation (18), the value of the liquid-free gas-flow rate, V, is :—

$$V = \frac{635N^2}{\sqrt{GT}} \times \sqrt{0{\cdot}45P^2 + 0{\cdot}1P_1P - 0{\cdot}55\,P_1^2}\ \text{cu. ft/day}$$

where P = upstream pressure, p.s.i.a., and P_1 = downstream pressure, p.s.i.a.

Hence $V = \dfrac{635N^2}{\sqrt{GT}} \times P\sqrt{E}$, where $\sqrt{E} = \sqrt{\left(1 - \dfrac{P_1}{P}\right)\left(0{\cdot}45 + \dfrac{0{\cdot}55P_1}{P}\right)}$

Evaluations of $\sqrt{E}$ are given in Table III and Fig. 2.

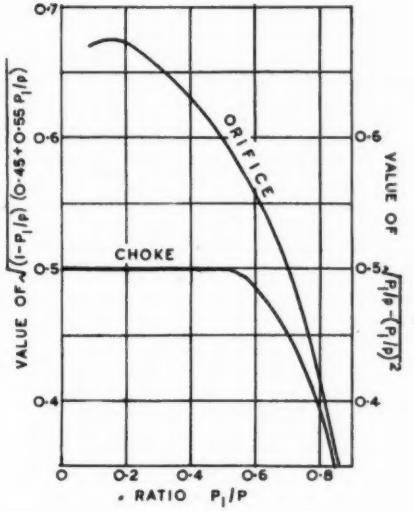

FIG. 2.

Hence, averaging by integration, the mean liquid-free gas rate, V_m, is given by :—

$$V_m = \frac{635N^2}{2\sqrt{GT}\,(P_A - P_B)}\left[(P_A + 0{\cdot}11P_1)P_A\sqrt{E_A} - (P_B + 0{\cdot}11P_1) \times P_B\sqrt{E_B} - 1{\cdot}97P_1^2 \log_{10} \frac{P_A\left(1 + \dfrac{\sqrt{E_A}}{0{\cdot}67}\right) + 0{\cdot}11P_1}{P_B\left(1 + \dfrac{\sqrt{E_B}}{0{\cdot}67}\right) + 0{\cdot}11P_1}\right] \text{cu. ft/day} \quad (20)$$

For Chokes (about 6 in uniform bore):

Choke:

(a) *Critical flow only*:

$$V = \frac{357N^2}{\sqrt{GT}}\left(1+\sqrt{\frac{N-1}{19}}\right) \times P, \text{ cu. ft/day.} \quad \text{(See Equation (16))}$$

where $P > 2P_1$.

Hence V_m, for $(P_B > 2P_1)$

$$= \frac{1}{(P_A - P_B)} \times \frac{357N^2}{\sqrt{GT}}\left(1+\sqrt{\frac{N-1}{19}}\right) \times \frac{(P_A^2 - P_B^2)}{2}$$

$$\therefore \quad V_m \text{ (Critical)} = \frac{357N^2}{\sqrt{GT}}\left(1+\sqrt{\frac{N-1}{19}}\right) \times \frac{(P_A + P_B)}{2} \text{ cu. ft/day} \quad (21)$$

where $P_B > 2P_1$.

(b) *Chokes*:

Non-critical flow only: $P_A < 2P_1$

$$V = \frac{357N^2}{\sqrt{GT}} \times \left(1+\sqrt{\frac{N-1}{19}}\right) \times 2 \times \sqrt{PP_1 - P_1^2} \text{ cu. ft/day.}$$

(See Equation (17).)

$$\therefore \quad \text{Average value, } V_m = \frac{1}{(P_A - P_B)} \times \frac{357N^2}{\sqrt{GT}}\left(1+\sqrt{\frac{N-1}{19}}\right) \times$$

$$\frac{4}{3P_1}\left[(P_AP_1 - P_1^2)^{3/2} - (P_BP_1 - P_1^2)^{3/2}\right] \text{ cu. ft/day} \quad . \quad (22)$$

where $P_A < 2P_1$.

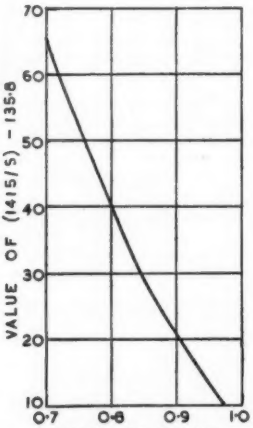

FIG. 3.

(c) *Chokes*: *combined critical and non-critical*: $P_A > 2P_1 > P_B$

$$\text{Average, } V_m = \frac{357N^2\left(1+\sqrt{\frac{N-1}{19}}\right)}{(P_A - P_B)\sqrt{GT}}\left[\frac{(P_A{}^2 - 4P_1{}^2)}{2} + \frac{4}{3P_1}(P_1{}^3 - (P_BP_1 - P_1{}^2)^{3/2})\right] \text{ cu. ft/day} \quad . \quad (23)$$

The gas–liquid ratio can be estimated by using Equation (19), together with the formula for V_m, which applies to the type of choke and flow,

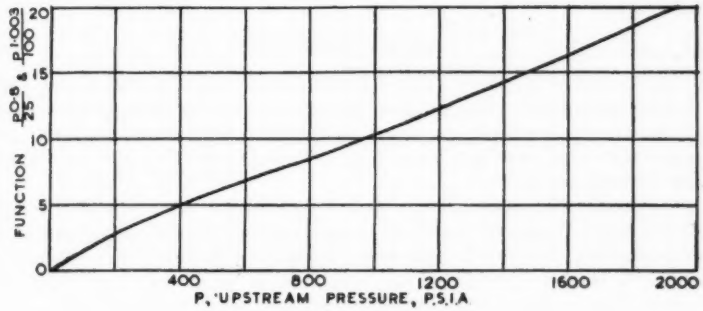

FIG. 4.

provided that the maximum and minimum values of tubing-head pressure and the ratios of duration of gas and oil to that of cycle, are known. In cases, where flows cease during the cycle, P_B equals P_1 in the equations for V_m.

TABLE V.

Well.	Durations.			Average production.		Pressures.			Orifice dia., N in $\frac{1}{64}$ in.	S/G.	V_m.	Gas–liquid ratio.	
	t_g.	t_o.	t_c.	Oil, b.d.	Gas, cu. ft/day.	P_a.	P_b.	P_1.				Calculated.	Measured.*
A	4·25	12·75	17	68	94,000	575	555	235	4	1·24	17,550	1,220	1,380
B	9·5	5	14·5	80	75,000	215	115	30	5·9	1·29	119,600	1,050	940
C	1·75	2·25	5·70	35	62,000	385	275	275	6	1·25	122,000	1,400	1,780†
D	1·1	1·80	2·9	144	390,000	860	805	275	6	1·23	611,000	2,680	2,710

* Meter readings uncorrected for inertia and "damping."
† Meter failed to read zero, due to "damping"; bad meter error.

RESULTS.

Table I and Table V show a comparison between the gas–oil ratios by actual measurement and calculation. The examples have been selected in order to present a wide range of the variables involved (*i.e.*, ratio, tubing-head pressure, pressure ratio, choke size, and oil-production rate).

It has been found that for local conditions this method of estimation of gas–liquid ratios is reasonably accurate. Even in cases where there is

appreciable variation in pressure due to slugging, the results are fairly accurate, if a true average of V is used in the calculation. In many cases due to damping of meters, the calculated ratios were more accurate than the metered ones.

The comparisons have been limited unavoidably to a small range in specific gravities of oil and gas. It would be interesting to learn what degree of accuracy can be attained in estimation with other ranges of specific gravities. Many assumptions have been made in order to simplify the equations; they are justified so far as local conditions are concerned by the accuracy attained in estimation of gas–liquid ratios, but it may, however, be found that they are not fully warranted where conditions are widely different.

Acknowledgements.

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The author also acknowledges his indebtedness to Mr J. C. Diehl and the Metric Metal Works of American Meter Co. Inc., for the data, from which the equations for liquid-free gas flow through the chokes have been derived; to Mr C. Beal for graphs of gas solubility in crude oil, from which the approximate equations for solubility have been derived empirically.

References.

[1] Diehl, J. C. "Natural Gas Handbook," published by Metric Metal Works, American Meter Co. Inc., 1927.

[2] Beal, C. "The Viscosity of Air, Water, Natural Gas, Crude Oil and its Associated Gases at Oilfield Temperatures and Pressures," *Petrol. Tech.* (*A.I.M.M.E.*), March 1946, **9** (2), Tech. Pub. No. 2018, 1–22.

THE INSTITUTE OF PETROLEUM.

SPECIAL GENERAL MEETING.

A SPECIAL GENERAL MEETING of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on May 11, 1949. THE PRESIDENT (Mr E. A. Evans) presided. The Agenda was :

To consider and if thought fit to pass with or without amendment the following resolutions, namely :—

(1) That By-Law number 37 be altered in the following manner :—

By substituting for the annual subscription to be paid by Members, Fellows, Associate Members, and Associate Fellows the following revised subscriptions, namely :—

Members	£4 4 0
Fellows	£4 4 0
Associate Members	£3 3 0
Associate Fellows	£3 3 0

(2) That By-Law number 37 as amended, and as set out below, is hereby approved and adopted as part of the By-Laws of the Institute, in substition for and to the exclusion of the existing By-Law number 37.

REVISED BY-LAW 37

"The following shall be the Annual Subscription to be paid for the classes of membership named :—

Hon. Members and Hon. Fellows	Nil
Members	£4 4 0
Fellows	£4 4 0
Associate Members	£3 3 0
Associate Fellows	£3 3 0
Member-Companies	Minimum £10 10 0
Collective Members	£10 10 0
Affiliated Members	As may be determined by Council
Student Members	£1 1 0

The Council shall have the power to reduce or to remit the Annual Subscription of a Corporate Member who has attained the age of 60 and who has retired from active participation in the petroleum or allied industries, or of any Corporate or Non-Corporate Member who shall have become temporarily unable to continue the subscription due from him."

(3) That the amended By-Law as in (2) above shall become effective on January 1, 1950.

THE GENERAL SECRETARY (D. A. Hough) read the notice convening the meeting.

THE PRESIDENT : We are here to discuss proposed changes in the By-Laws, and I will call on Mr Hyams to give the reasons for the changes.

MR H. HYAMS (Chairman, By-Laws and Finance Committees) : In presenting for your approval the three resolutions which appear on the agenda paper I feel you should know certain facts as to the reasons which prompted Council to ask for these revisions of the By-Laws :—

(1) Despite mounting increases in the cost of operating the Institute, the subscription rates for Corporate Members have remained unaltered,

so far as I can trace in the Institute's records. Although our membership has almost doubled since 1930 (we have now some 2400 members), the income per member has remained stationary. In 1930 we received an average of £2 13*s*. per head, in 1938 £2 15*s*., and in 1948 £2 14*s*.

(2) The expansion in our activities has resulted in the need for a larger and better-balanced staff as well as extended premises. These, together with all-round increases in costs, are reflected in the very substantial rise in our operating expenditure. For example, our salaries and wages bill this year will be £7500, compared with less than half that sum in 1946. We now pay £2500 rent for our premises at Manson House. In 1945–47 we paid only £375.

(3) You should be aware of some figures relating to the cost of providing you with two regular publications—the *Journal* and the *I.P. Review*. In terms of pages of printed matter we are now supplying you with 40 per cent more material in the two monthly publications than we did in 1938. But we shall be spending £7500 this year in printing and posting the two publications to you, including the provision of the Abstracts. In 1945, when we produced the *Journal* only, we spent only one-third of this sum—£2500. The new *I.P. Review* accounts for only part of this 300 per cent increase; increased costs of printing, illustrations, and paper take care of the remainder.

You will be interested to know that if we add a reasonable amount for salaries and office overheads to the cost of producing the two journals, the expense incurred by the Institute in supplying each Corporate Member and Student with the two publications works out at £2 10*s*. per annum—nearly the whole of the present income from the average member.

(4) All these figures lead me to the statement that expenditure has so far exceeded income in recent years that our Reserves in Revenue Account were down to £2600 at the end of last year. We have consumed £4130 of our reserves in the last three years. Had we not arranged to introduce the new grade of Member-Company some months ago, our deficit for 1949 would have been about £7000, and by this time we should have completely eaten up our liquid reserves, necessitating our looking for some means of raising money to keep the Institute going.

Your Council is satisfied that the activities of the Institute in its various fields should not be reduced and that the money required to operate efficiently should be found. It is hoped that the major part of the additional revenue of some £7000 to £8000 per annum will be forthcoming from Member-Companies, but your Council feels that Corporate Members, because of the facilities and opportunities we provide, should bear a small share of the very substantial increase in operating costs to which I have referred.

Approval of our proposals to increase the subscriptions of Fellows and Members by one guinea and those of Associate Fellows and Associate Members by half-guinea will yield an additional annual income of about £1500, only about 20 per cent of the supplementary revenue we require to balance our budget. I would add that we are one of the last of the scientific and technical organizations to increase our subscription rates, and that your Council is satisfied that the proposed increases are equitable and modest in the circumstances which I have briefly outlined.

Mr President: I have pleasure in submitting for the approval of this Special General Meeting Resolutions 1, 2, and 3 as they appear on the Agenda paper, and to propose that the amended By-Law No. 37 as set out in Resolution No. 2 be hereby approved and adopted, to take effect as from January 1, 1950.

Mr V. Biske (Member of Council): Normally one has pleasure in proposing or seconding a resolution. I will be quite honest in this case and say that I do not think one has much pleasure in proposing these resolutions, but Mr Hyams has told us that it is in the interests of the Institute that the resolutions should be passed.

The resolutions are in two portions, and there is a separate portion as to the date at which the proposed amended By-Law comes into effect. The "appointed day" will be January 1, 1950.

I second that the resolutions amending the By-Laws be passed by the meeting.

Dr R. F. Goldstein: May I say that I support these resolutions. But I should like to ask for information on the publications side, as to whether the advertisement revenue has grown *pro rata* with the cost of printing, and whether, allowing for that revenue, the *Journal* is earning money.

Mr Hyams: I can answer the first part of the question. As to the second part, I shall require some notice—to use a Parliamentary phrase.

In the last two years we considered very carefully the advertisement rates charged by the Institute, and we were satisfied that the rates are in line with those which are obtained elsewhere. In that sense our income from advertisements has definitely gone up and, so far as paper limitations will allow, that point is still under very active consideration, because there may be a possibility of increasing the size of the *I.P. Review* as a result of a larger paper allocation.

As to the second part of the question, I shall be only too happy to supply the questioner with further information by correspondence if he will give me time to look out the figures.

There being no further discussion, the President put the resolutions to the meeting and they were carried unanimously.

The business of the Special General Meeting was then closed.